

# Argonne National Laboratory

## SOME TOPICS IN STATISTICAL MECHANICS

A Series of Lectures by

B. R. A. Nijboer

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ARGONNE NATIONAL LABORATORY  
9700 South Cass Avenue  
Argonne, Illinois 60440

SOME TOPICS IN STATISTICAL MECHANICS  
(Molecular distribution functions, cluster expansions, etc.)

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B. R. A. Nijboer

Solid State Science Division

June 1965

Operated by The University of Chicago  
under  
Contract W-31-109-eng-38  
with the  
U. S. Atomic Energy Commission





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# SOME TOPICS IN STATISTICAL MECHANICS

(Molecular distribution functions, cluster expansions, etc.)

by

B. R. A. Nijboer

## I. INTRODUCTION

### A. Literature

These lectures will deal mainly with the pair distribution function, its definition, its properties, and its cluster expansion. The principal aim of these lectures is to give enough basic information to enable anyone who is interested in specific applications to find his way in the recent literature.

Let me first mention some books and review articles where one may find more about the subject we are going to treat:

- 1) I. Z. Fisher, Statistical Theory of Liquids, The University of Chicago Press (1964); translated from the original Russian edition, with a supplement by S. A. Rice and P. Gray.
- 2) J. de Boer, Molecular Distribution and Equation of State of Gases, Reports on Progress in Physics 12, 305 (1949).
- 3) E. G. D. Cohen, ed., Fundamental Problems in Statistical Mechanics, NUFFIC Summer School, 1961, North Holland Publishing Company, Amsterdam (1962).
- 4) G. E. Uhlenbeck and G. W. Ford, Lectures in Statistical Mechanics, Proc. Summer Seminar, Boulder, 1960, Am. Math. Soc., Providence (1963).
- 5) G. E. Uhlenbeck, Statistical Physics 3, Brandeis Summer Institute, 1962, W. A. Benjamin, Inc., New York, (1963).
- 6) J. de Boer and G. E. Uhlenbeck, ed., Studies in Statistical Mechanics, Vols. I and II, North Holland Publishing Company, Amsterdam (1962 and 1964).
- 7) H. L. Frisch and J. L. Lebowitz, ed., The Equilibrium Theory of Classical Fluids, a lecture note and reprint volume, W. A. Benjamin, Inc., New York (1964).

Further, of course, one may find some of our topics treated in the usual textbooks on statistical mechanics, among which I wish to mention in particular:

T. L. Hill, Statistical Mechanics, McGraw-Hill, New York (1956).

J. E. Mayer and M. G. Mayer, Statistical Mechanics, John Wiley and Sons, Inc., New York (1940).

A. Münster, Statistische Thermodynamik, Springer, Berlin (1956).

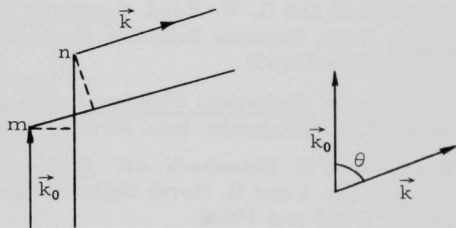
## B. The Paper of F. Zernike and J. Prins

Before starting with a more systematic treatment, I would like to give a short review of the classical paper by F. Zernike and J. Prins, *Z. Physik* 41, 184 (1927). The reasons for doing this are: a) In this paper, the radial distribution function  $g(r)$  was first introduced in theoretical physics, and its importance for the theory of scattering was clearly realized. b) The  $g(r)$ -function was calculated here for a particularly simple system, viz., the one-dimensional hard-sphere system. This system is one of the very few for which  $g(r)$  can at all be computed rigorously.

Let us consider the scattering of X rays by a monatomic fluid. The wave vector of the incoming plane wave is  $\vec{k}_0$ , and we want to calculate the differential cross section for scattering in a direction given by the outgoing wave vector  $\vec{k}$  ( $k = k_0$ ). Let the scattering amplitude for one atom be  $a$ . For the differential cross section per particle, we have

$$\sigma(\theta) = N^{-1} a^2 \sum_n \sum_m e^{i\vec{k} \cdot (\vec{r}_n - \vec{r}_m)}. \quad (\text{I-1})$$

Here,  $\vec{\kappa} = \vec{k}_0 - \vec{k}$ ,  $N$  is the number of particles, and  $\vec{r}_n$  and  $\vec{r}_m$  are the positions of particles  $n$  and  $m$  respectively. The exponent  $\vec{\kappa} \cdot (\vec{r}_n - \vec{r}_m)$  gives the phase difference between the waves scattered at  $n$  and  $m$ . (See sketch below.)



The expression (I-1) must be averaged over the configurations of the scattering system. One obtains, when taking the terms with  $n = m$  apart,

$$\sigma(\theta) = a^2 \left\{ 1 + \rho \int [g(\vec{r}) - 1] e^{i\vec{\kappa} \cdot \vec{r}} d\vec{r} \right\}. \quad (\text{I-2})$$



This is the famous formula of Zernike and Prins. Here  $\rho = N/V$  is the average density (number of particles per unit volume), and  $g(\vec{r})$  is the pair distribution function, somewhat loosely defined as follows:  $\rho g(\vec{r})$  is the average density at position  $\vec{r}$  if we know that a particle is at the origin, or also  $g(\vec{r}_1 - \vec{r}_2)(d\vec{r}_1/V)(d\vec{r}_2/V)$  is the probability of finding particle 1 in volume element  $d\vec{r}_1$  and at the same time particle 2 in  $d\vec{r}_2$ . The pair distribution function measures the correlation between pairs of particles. For a system of noninteracting particles (ideal gas),  $g(\vec{r}) = 1$  for all  $\vec{r}$ , while in any fluid,  $g(\vec{r})$  approaches 1 for large  $\vec{r}$ . We have subtracted 1 from  $g(\vec{r})$  in the above formula. This term amounts to  $8\pi^2\rho\delta(\vec{\kappa})$ , which is different from zero only for  $\theta = 0$ . It represents the unscattered beam. The integral may now be extended over an infinite volume. If we express  $\sigma(\theta)$  or  $\sigma(\vec{\kappa})$  in units  $a^2$  (differential cross section of one isolated particle), we see that  $\sigma(\vec{\kappa}) - 1$  is the Fourier transform of  $\rho(g(\vec{r}) - 1)$ . Conversely,  $g(\vec{r})$  may, in principle, be obtained from the X-ray diffraction pattern.

I would like to add a few remarks here. In the derivation, we supposed the particles fixed and then averaged over their configuration with the true statistical distribution function. Nowadays one calls it the static approximation. It is valid for X rays, because in this case the energy transfer can be neglected compared to the primary energy. For slow-neutron scattering, the primary energy and the energy transfer are of the same order. In this case, the static approximation is no longer valid. One can then investigate the more detailed scattering function  $S(\vec{\kappa}, \omega)$ , where  $\hbar\omega$  is the energy transfer. One can show that for

$$\int_{-\infty}^{+\infty} S(\vec{\kappa}, \omega) d\omega,$$

the static approximation still holds. However, this integral is no longer exactly equal to the differential cross section  $\sigma(\theta)$ , because for fixed  $\theta$ ,  $\vec{\kappa}$  is no longer a constant vector.

For the case of scattering of light, where the wavelength  $\lambda$  is much larger than the distance over which  $g(r) - 1$  is different from zero (except near critical conditions), one may replace  $e^{i\vec{\kappa}\cdot\vec{r}}$  by 1. One then has

$$\frac{\sigma(\theta)}{a(\theta)^2} = 1 + \rho \int \{g(\vec{r}) - 1\} d\vec{r}. \quad (\text{I-3})$$

We will show later that the right-hand side is

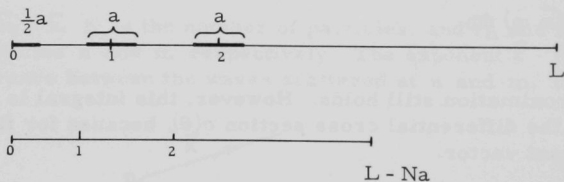
$$1 + \rho \int \{g(\vec{r}) - 1\} d\vec{r} = \frac{\langle n_{\Omega}^2 \rangle - \langle n_{\Omega} \rangle^2}{\langle n_{\Omega} \rangle} = kT \left( \frac{\partial \rho}{\partial p} \right)_T \equiv \chi_T. \quad (\text{I-4})$$

This is the formula of Ornstein and Zernike. It expresses our integral in terms of the density fluctuations ( $\Omega$  is an arbitrary volume, containing many particles, but small compared to the total volume);  $\chi_T$  is the relative isothermal compressibility of the system, i.e., the isothermal compressibility divided by that of an ideal gas of the same density.

Let us now calculate  $g(x)$  for a one-dimensional system of hard spheres or rather hard rods. Suppose we have a line of length  $L$  upon which are  $N$  rods, each of length  $a$ . The position of each rod is represented by its center. We now ask for the probability of finding another center at a distance between  $x$  and  $x + dx$  from a given center. This is clearly  $\rho g(x) dx$ . One has  $g(-x) = g(x)$  and  $g(x) = 0$  for  $x < a$ . For  $a < x < 2a$ , there is, at most, one particle on the length  $x$ ; for  $ka < x < (k+1)a$ , the number of particles on the line of length  $x$  (starting from a given particle) is at most  $k$ . One may now put

$$g(x) = \sum_k g_k(x), \quad (I-5)$$

where  $\rho g_k(x) dx$  is the probability that the  $k$ th atom (numbered from the given particle at  $x = 0$ ) may be found between  $x$  and  $x + dx$ . For any  $x$ , the number of terms in the sum (I-5) is finite. It is now convenient to look only at the intervals between particles. If we subtract the volume of the atoms, we have a line of Length  $L - Na$ , and hereupon  $N$  points distributed at random, as shown below:



Our problem is now analogous to that of the distribution of free paths in gas theory. The probability of finding an interval of length  $x'$  is (Clausius)

$$\frac{1}{\ell} e^{-x'/\ell} \quad (I-6)$$

when  $L \rightarrow \infty$  and  $N \rightarrow \infty$  in such a way that  $(L - Na)/N = \ell$ . We see that  $\ell$  is the mean length of the interval.

Let us recall briefly the derivation of (I-6). The probability of finding a given point on a segment of length  $x'$  is  $x'/(L - Na)$ . The probability that this segment will contain no particles is

$$\left(1 - \frac{x'}{L - Na}\right)^N = \left(1 - \frac{x'}{N\ell}\right)^N.$$

This expression approaches  $e^{-x'/\ell}$  when  $N \rightarrow \infty$ . The probability then of finding an interval with length between  $x'$  and  $x' + dx'$  is  $e^{-x'/\ell} \cdot dx'/\ell$ .

From (I-6), it follows that the probability that the sum of two adjacent intervals lies between  $x'$  and  $x' + dx'$  is

$$dx' \int_0^{x'} \frac{1}{\ell} e^{-x''/\ell} \frac{1}{\ell} e^{-(x' - x'')/\ell} dx'' = \frac{x'}{\ell^2} e^{-x'/\ell} dx'.$$

Similarly, one finds for the probability that the total length of  $k$  adjacent intervals is between  $x'$  and  $x' + dx'$

$$\rho g_k(x') dx' = \frac{x'^{k-1}}{\ell^k (k-1)!} e^{-x'/\ell} dx'. \quad (\text{I-7})$$

One verifies that

$$\sum_{k=1}^{\infty} \rho g_k(x') dx' = \frac{dx'}{\ell},$$

as it should.

Returning now to the problem of the rods, we have at each point to add in a length  $a$ . For  $g_k$ , one has  $x = x' + ka$ , and therefore

$$\begin{aligned} \rho g_k(x) &= \frac{(x - ka)^{k-1}}{\ell^k (k-1)!} e^{-(x-ka)/\ell}, & \text{for } x > ka; \\ &= 0, & \text{for } x < ka; \end{aligned}$$

so that finally

$$\rho g(x) = \frac{1}{\ell} \left\{ e^{-(x-a)/\ell} + \frac{x-2a}{\ell \cdot 1!} e^{-(x-2a)/\ell} + \frac{(x-3a)^2}{\ell^2 \cdot 2!} e^{-(x-3a)/\ell} + \dots \right\}, \quad (\text{I-8})$$

where the sum should be continued as long as the exponents are negative. This is the result of Zernike and Prins. In their paper, they plotted  $g(x)$  as a function of  $x$  for the cases  $\ell = 0.5, 0.25$ , and  $0.1$  ( $1/\rho = \ell + a$  is taken to be 1). The smaller  $\ell$ , the higher-peaked is  $g(x)$  and the farther do the correlations extend.

The expression (I-8) for  $\rho g(x)$  is a rather complicated one. However, it is worth mentioning that its Laplace transform is very simple. We have, namely,

$$\rho \tilde{g}_k(s) \equiv \int_0^{\infty} e^{-sx} \rho g_k(x) dx = \frac{e^{-ska}}{(sl+1)^k}, \quad (\text{I-9})$$

and therefore

$$\rho \tilde{g}(s) \equiv \int_0^{\infty} e^{-sx} \rho g(x) dx = \sum_1^{\infty} \frac{e^{-ska}}{(sl+1)^k} = \frac{1}{(sl+1) e^{sa} - 1}. \quad (\text{I-10})$$

From

$$\lim_{s \rightarrow 0} \rho \tilde{g}(s) = \frac{1}{s(\ell + a)},$$

it follows that

$$\lim_{x \rightarrow \infty} \rho g(x) = \frac{1}{\ell + a}.$$

Furthermore, in (I-10) it is easy to go to the limit  $\ell \rightarrow 0$ , which is not so simple in  $g(x)$ . We have

$$\lim_{\ell \rightarrow 0} \rho \tilde{g}(s) = \frac{1}{e^{sa} - 1},$$

from which it follows that

$$\lim_{\ell \rightarrow 0} \rho g(x) = \sum_{k=1}^{\infty} \delta(x - ka). \quad (\text{I-11})$$

One sees here the transition from gas to liquid to crystal. However, this transition is perfectly continuous; in one dimension, there are no phase transitions. This unconventional method to derive the expression for  $g(x)$  cannot, unfortunately, be applied to other systems or to the three-dimensional hard-sphere system. We shall now turn to a more systematic treatment in terms of statistical mechanics of the pair distribution function. We shall see that starting from the general definition it is also possible to derive the above result (I-8) for the one-dimensional hard-sphere system, though the derivation is rather more complicated.



## II. ENSEMBLES AND THE LIOUVILLE THEOREM

Let us start recalling some basic concepts of statistical mechanics. The aim of statistical mechanics is to establish relations between the observable macroscopic properties of large systems (containing a very large number of atoms) and the properties of the particles and their interactions as given by atomic theory. Statistical mechanics tries to provide an atomistic foundation of the phenomenological laws established in thermodynamics and other fields of macroscopic physics.

A macroscopic quantity of matter contains of the order of  $10^{20}$  atoms. Suppose we may consider the system classically; then from precise positions and momenta of all particles at time  $t = 0$ , one could, in principle, calculate the exact state of the system at some other time  $t$ . We do not have this detailed information, and the computations would be hopelessly complicated. Further, we are not really interested in the position and velocity of every atom at some later time. We are only interested in a relatively small number of so-called macroscopic quantities which can be measured. Consider, for example, the pressure of a gas. The forces exerted by the molecules on the walls of the container vary extremely rapidly. We only want to know some average of this force over small space and time regions. It is evident that for this purpose, statistical arguments have to be invoked.

We will mainly restrict ourselves to classical statistical mechanics and to systems in equilibrium. Let us suppose we have a system consisting of a very large number  $N$  of identical molecules, the motions of which can be described by a Hamiltonian,

$$H = \sum_i \frac{\vec{p}_i^2}{2m} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \quad (\text{II-1})$$

The state of the system is then completely specified by a point in the  $6N$ -dimensional phase space, the so-called  $\Gamma$ -space (Ehrenfest). The representative point describes a path in  $\Gamma$ -space according to the Hamiltonian equations of motion,

$$\left. \begin{aligned} \dot{q}_k &= \frac{\partial H}{\partial p_k}, \\ \text{and} \\ \dot{p}_k &= -\frac{\partial H}{\partial q_k}. \end{aligned} \right\} \quad (\text{II-2})$$

This path is of extreme complexity; if two molecules collide, the representative point jumps from one region to another. Since in each point the direction of the tangent to the path is uniquely given by the above equations of motion, a path can never cross itself. If the system is isolated, the total energy is conserved and the phase point moves on the so-called energy surface.

In statistical mechanics, one now considers not one system, but one imagines a very large number of identical systems, which is called an ensemble. The systems are supposed to differ only in phase; i.e., the initial conditions are different. We have, therefore, a cloud of phase points moving in  $\Gamma$ -space. Two orbits never cross. An ensemble is characterized by a density  $\rho(q_1, \dots, p_{3N}, t)$ , which we suppose to be normalized; i.e.,

$$\int \rho(q_1, \dots, p_{3N}, t) dq_1 \dots dp_{3N} = 1. \quad (\text{II-3})$$

The function  $\rho$  cannot be an arbitrary function subject to (II-3). First we have  $\rho \geq 0$ , and further

$$\frac{\partial \rho}{\partial t} + \sum_k \frac{\partial}{\partial q_k} (\dot{q}_k \rho) + \sum_k \frac{\partial}{\partial p_k} (\dot{p}_k \rho) = 0. \quad (\text{II-4})$$

This is the equation of continuity, expressing the fact that the increase of the number of phase points in an arbitrary volume element of phase space during some time interval must be equal to the number of phase points entering through its boundary during that time. If we integrate (II-4) over all phase space, we find that

$$\int \rho(q_1, \dots, p_{3N}, t) dq_1 \dots dp_{3N}$$

remains constant in time, so that if (II-3) holds at any moment,  $\rho$  will stay normalized in the course of time. Equation (II-4) may be written

$$\frac{\partial \rho}{\partial t} + \sum_k \dot{q}_k \frac{\partial \rho}{\partial q_k} + \sum_k \dot{p}_k \frac{\partial \rho}{\partial p_k} + \sum_k \rho \left( \frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right) = 0. \quad (\text{II-5})$$

The last term cancels because of the equations of motion (II-2). We find, therefore,

$$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \sum_k \dot{q}_k \frac{\partial \rho}{\partial q_k} + \sum_k \dot{p}_k \frac{\partial \rho}{\partial p_k} = \frac{\partial \rho}{\partial t} + (\rho, H) = 0, \quad (\text{II-6})$$

where

$$(\rho, H) \equiv \sum_k \left( \frac{\partial \rho}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial \rho}{\partial p_k} \frac{\partial H}{\partial q_k} \right)$$

is the Poisson-bracket. This is the equation of Liouville. It states that  $\rho$  is conserved as we move with the phase points, or also that the phase points move as an incompressible fluid. It is a consequence of the equations of motion. One might also say that the extension in phase space is conserved; i.e., if we consider a cloud of given volume in  $\Gamma$ -space and follow its motion, then the volume occupied at some later time is equal in size, though generally very different in shape. Liouville is sometimes expressed as

$$\frac{\partial(q_1, \dots, p_{3N})}{\partial[q_1(0), \dots, p_{3N}(0)]} = 1, \quad (\text{II-7})$$

which is equivalent to the above formulation.

The fundamental assumption of statistical mechanics is that the macroscopic quantities as measured on a system correspond to the ensemble average taken over a suitably chosen ensemble,

$$\langle f(q_1, \dots, p_{3N}) \rangle = \int f \rho \, dq_1 \dots dp_{3N}. \quad (\text{II-8})$$

For a system in equilibrium, where the macroscopic properties do not depend on time,  $\rho$  may not explicitly depend on time; i.e., the equilibrium ensemble should be stationary.

According to Liouville,  $\rho$  remains constant when moving with the phase points, so that for a stationary ensemble  $\rho(q_1, \dots, p_{3N})$  should be chosen at some initial time in such a way that it is the same all along the orbit. This means that for a stationary ensemble,  $\rho$  may depend on the integrals of motion only. In practice, one only considers the case that  $\rho$  depends exclusively on the value of the total energy  $E$ . Other integrals of motion are usually not known. The best-known stationary ensembles are:

(a) Microcanonical ensemble (Boltzmann). Here,  $\rho$  is taken to be a constant between two neighboring energy surfaces and zero everywhere else. If the difference in energy between the surfaces approaches zero, one has a so-called surface ensemble with surface density  $\propto |\text{grad } E|^{-1}$ .

(b) Canonical ensemble (Gibbs). Here,

$$\rho = \text{constant} \cdot e^{-\frac{H(p_1, \dots, q_{3N})}{kT}}.$$

(c) Grandcanonical ensemble (also introduced by Gibbs). We will come back to this later.

For most practical purposes, the various ensembles mentioned above lead to equivalent results. Usually the microcanonical ensemble is considered to represent an isolated system for which the energy is conserved, and the canonical ensemble is considered to represent a system in contact with a large heat bath. Here the temperature is fixed and the energy fluctuates. The canonical ensemble is often much more convenient than the microcanonical, because in the latter the integration over phase space necessary to compute averages has to be restricted to the energy surface, which may be rather awkward. Darwin and Fowler consider the canonical ensemble as just a mathematical device to make the calculation of averages easier. In the canonical ensemble, the actual spread in energy is extremely small for large systems; that is, the overwhelming number of systems has an energy very close to the mean value. This is because for a large system the volume of phase space between two successive energy shells increases with a large power of  $E$ . Let us take as an example the average energy. In the canonical ensemble, it can be expressed as

$$\langle E \rangle = \left\{ \int \Omega(E) e^{-E/kT} dE \right\}^{-1} \cdot \int E \Omega(E) e^{-E/kT} dE, \quad (\text{II-9})$$

where  $\Omega(E) dE$  is the volume of phase space between the energy shells  $E$  and  $E + dE$ . For an ideal gas, one easily verifies that  $\Omega(E) \propto E^{(3/2)N-1}$ . Now the function  $E^\nu e^{-E/kT}$  has for large  $\nu$  a very sharp maximum for  $E = \nu kT$ . If we put  $E = \nu kT x$ , then

$$E^\nu e^{-E/kT} = \left( \frac{\nu kT}{e} \right)^\nu (x e^{1-x})^\nu.$$

Now  $x e^{1-x} = 1$  for  $x = 1$ , and  $x e^{1-x} < 1$  for all other positive  $x$ . The large power of  $x e^{1-x}$  makes the maximum extremely sharp. In this sense, the energy of the system becomes a unique function of its temperature.

In the following, we will mainly use the canonical ensemble. Let us conclude this chapter with a few remarks.



## Remarks

1. We derived the equation of Liouville for the change with time of the density of phase points in  $\Gamma$ -space. This equation in itself has nothing to do with statistical mechanics; it belongs to mechanics proper. It is perfectly reversible in time, i.e., invariant for the transformation  $t \rightarrow -t$ . One of the fundamental problems in statistical mechanics is how to arrive from Liouville to an irreversible equation (like the Boltzmann equation or the master equation) from which the well-known irreversible behavior of actual macroscopic physical systems can be explained. For a very clear discussion of the justification of ensemble theory in equilibrium statistical mechanics and for an explanation of the apparently paradoxical irreversible behavior of macroscopic systems, I refer to Uhlenbeck and Ford, (Ref. 4) mentioned in Section I-A.

2. For any function in phase space  $f(q_1, \dots, p_N, t)$  we have

$$\frac{df}{dt} = \sum_k \left( \frac{\partial f}{\partial q_k} \frac{\partial H}{\partial p_k} - \frac{\partial f}{\partial p_k} \frac{\partial H}{\partial q_k} \right) + \frac{\partial f}{\partial t} = \frac{\partial f}{\partial t} + (f, H) = Lf, \quad (\text{II-10})$$

where

$$L = \frac{\partial}{\partial t} + \sum_k \left( \frac{\partial H}{\partial p_k} \frac{\partial}{\partial q_k} - \frac{\partial H}{\partial q_k} \frac{\partial}{\partial p_k} \right)$$

is called the Liouville operator. The equation (II-10) can be integrated formally giving

$$f(t) = e^{Lt} f(0), \quad (\text{II-11})$$

for then

$$\frac{df}{dt} = Le^{Lt} f(0) = Lf(t).$$

### III. MOLECULAR DISTRIBUTION FUNCTIONS

Let us consider an arbitrary stationary ensemble. We have introduced the density  $\rho_N(\vec{r}_1, \dots, \vec{p}_N)$ , so that  $\rho d\tau$  is the probability of finding a system of the ensemble in the volume element  $d\tau$  of  $\Gamma$ -space. According to the fundamental assumption of statistical mechanics, this also represents the probability of finding, during the time of observation, our physical system in the element  $d\vec{r}_1 \dots d\vec{p}_N$  of  $\Gamma$ -space, i.e., the probability of finding particle 1 in  $d\vec{r}_1 d\vec{p}_1$ , particle 2 in  $d\vec{r}_2 d\vec{p}_2$ , etc., in  $\mu$ -space ( $\mu$ -space is the six-dimensional phase space of one molecule). From  $\rho_N$  we can, in principle, calculate all macroscopic properties of our system;  $\rho_N$  still characterizes the system in great detail. Usually, however, one does not need such detailed information; one usually wants to average only quantities which are a sum of one-particle or two-particle functions. These averages can be calculated as soon as one knows reduced distribution functions, e.g., one-particle or two-particle distribution functions. We shall soon meet with examples.

We then introduce reduced distribution functions, e.g.,

$$\rho_3(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{p}_1, \vec{p}_2, \vec{p}_3) = \int \rho_N(\vec{r}_1, \dots, \vec{p}_N) d\vec{r}_4 \dots d\vec{r}_N d\vec{p}_4 \dots d\vec{p}_N, \quad (\text{III-1})$$

which is the probability of finding three numbered molecules 1, 2, and 3 at  $d\vec{r}_1 d\vec{p}_1$ ,  $d\vec{r}_2 d\vec{p}_2$ , and  $d\vec{r}_3 d\vec{p}_3$ , respectively, not regarding where the other molecules are. If all molecules are of one kind, it is useful to introduce, instead of the specific distribution functions considered above, the so-called generic distribution functions  $P$ , where the molecules are left unspecified. These are

$$\left. \begin{aligned} P_N(\vec{r}_1, \dots, \vec{p}_N) &= N! \rho_N(\vec{r}_1, \dots, \vec{p}_N), \\ \text{and} \\ P_m(\vec{r}_1, \dots, \vec{p}_m) &= \frac{N!}{(N-m)!} \rho_m(\vec{r}_1, \dots, \vec{p}_m), \end{aligned} \right\} \quad (\text{III-2})$$

where  $N!/(N-m)!$  is the number of ways in which  $m$  molecules can be chosen out of  $N$ . In particular,

$$\left. \begin{aligned} P_2(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2) &= N(N-1) \rho_2(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2), \\ \text{and} \\ P_1(\vec{r}_1, \vec{p}_1) &= N \rho_1(\vec{r}_1, \vec{p}_1). \end{aligned} \right\} \quad (\text{III-3})$$

Finally, by integrating over momenta, one obtains either specific or generic distribution functions in configuration space only. For the generic functions in particular, we have

$$\left. \begin{aligned}
 n_N(\vec{r}_1, \dots, \vec{r}_N) &= \int P_N(\vec{r}_1, \dots, \vec{p}_N) d\vec{p}_1 \dots d\vec{p}_N = \\
 N! \int \rho_N(\vec{r}_1, \dots, \vec{p}_N) d\vec{p}_1 \dots d\vec{p}_N, \\
 \text{and} \\
 n_m(\vec{r}_1, \dots, \vec{r}_m) &= \int P_m(\vec{r}_1, \dots, \vec{p}_m) d\vec{p}_1 \dots d\vec{p}_m = \\
 \frac{N!}{(N-m)!} \int \rho_m(\vec{r}_1, \dots, \vec{p}_m) d\vec{p}_1 \dots d\vec{p}_m.
 \end{aligned} \right\} \quad (\text{III-4})$$

From these definitions, it will be obvious that the normalization of these functions is given by

$$\int n_m(\vec{r}_1, \dots, \vec{r}_m) d\vec{r}_1 \dots d\vec{r}_m = \frac{N!}{(N-m)!}. \quad (\text{III-5})$$

Also, it is easy to verify that, e.g.,

$$n_2(\vec{r}_1, \vec{r}_2) = \frac{1}{N-2} \int n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) d\vec{r}_3 = \frac{1}{(N-2)!} \int n_N d\vec{r}_3 \dots d\vec{r}_N, \quad (\text{III-6})$$

and

$$n_1(\vec{r}_1) = \frac{1}{N-1} \int n_2(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = \frac{1}{(N-1)!} \int n_N d\vec{r}_2 \dots d\vec{r}_N, \quad (\text{III-7})$$

or generally

$$n_m(\vec{r}_1, \dots, \vec{r}_m) = \frac{1}{N-m} \int n_{m+1}(\vec{r}_1, \dots, \vec{r}_{m+1}) d\vec{r}_{m+1}. \quad (\text{III-8})$$

$n_2(\vec{r}_1, \vec{r}_2)$  is called the two-particle (or sometimes pair-) distribution function;  $n_1(\vec{r}_1)$  is the number density. All this was perfectly general. Let us now specialize to a canonical ensemble. Here we have

$$\rho_N(\vec{r}_1, \dots, \vec{p}_N) = (h^{3N} N! Z_N)^{-1} e^{-\beta H(\vec{r}_1, \dots, \vec{p}_N)}. \quad (\text{III-9})$$

Here  $H$  is the Hamiltonian,  $\beta = 1/kT$ , and the factor in front with

$$Z_N = \frac{1}{N! h^{3N}} \int e^{-\beta H} d\vec{r}_1 \dots d\vec{p}_N \quad (\text{III-10})$$

is a normalizing factor. [The insertion of the factors  $N!$  and  $h^{3N}$  ( $h$  is Planck's constant) will be explained below.] The integration over momenta gives  $(2\pi mkT)^{3N/2}$ , so that [cf. (III-4) and (II-1)]

$$n_N(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{Q_N} e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} \quad (\text{III-11})$$

with

$$Q_N = \left( \frac{h^2}{2\pi mkT} \right)^{3N/2} Z_N = \frac{1}{N!} \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_1 \dots d\vec{r}_N. \quad (\text{III-12})$$

As a consequence, we have [cf. (III-6) and (III-7)]

$$n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{(N-3)! Q_N} \int e^{-\beta V} d\vec{r}_4 \dots d\vec{r}_N, \quad (\text{III-13})$$

$$n_2(\vec{r}_1, \vec{r}_2) = \frac{1}{(N-2)! Q_N} \int e^{-\beta V} d\vec{r}_3 \dots d\vec{r}_N, \quad (\text{III-14})$$

and

$$n_1(\vec{r}_1) = \frac{1}{(N-1)! Q_N} \int e^{-\beta V} d\vec{r}_2 \dots d\vec{r}_N. \quad (\text{III-15})$$

$Z_N$  is called the partition function,  $Q_N$  the configurational partition function. These are important concepts, because from them, all thermodynamic properties can be calculated via the (Helmholtz) free energy  $F = U - TS$ , which is given by



$$F = -kT \log Z_N = -(3/2) NkT \log \left( \frac{2\pi mkT}{h^2} \right) - kT \log Q_N. \quad (\text{III-16})$$

This correspondence between statistical and thermodynamic quantities can be shown to hold in various ways; one of them we will mention further on. The factors  $h^{3N}$  and  $N!$  in the definition (III-10) of  $Z_N$  have the following motivation. As to  $h^{3N}$ , a factor of this dimension is needed to make  $Z_N$  dimensionless; by putting in  $h^{3N}$  ( $h$  is Planck's constant), one obtains the same result for  $F$  as the classical limit of quantum statistics.  $N!$  is inserted so that the free energy becomes an extensive quantity (or, in other words, to make the entropy additive or to avoid the Gibbs paradox).

As a matter of fact, this correspondence with thermodynamics (or with macroscopic theory) has only sense in the so-called thermodynamic limit; i.e., where  $N \rightarrow \infty$ ,  $V(\text{volume}) \rightarrow \infty$  in such a way that  $\rho = N/V$  remains constant. Actually, one can prove, under certain restrictions for the interactions, that in this limit

$$\frac{1}{N} \log Z_N$$

exists and is independent of  $N$ . It then represents  $-1/kT$  times the free energy  $f$  per particle; i.e., in this limit,

$$e^{-\frac{Nf}{kT}} = \frac{1}{N!h^{3N}} \int e^{-\beta H} d\vec{r}_1 \dots d\vec{p}_N. \quad (\text{III-17})$$

The first proof of this statement was given by L. Van Hove (Physica, 1948; in this paper, it was also shown that  $p = -(\partial f / \partial v)_T$  is a nonincreasing function of the volume per particle  $v$ ). Later it was realized that the proof contained certain defects. Recent considerations on this topic are due, among others, to D. Ruelle (1963) (cf., e.g., Ref. 7).

In the definition of the distribution functions, one usually either explicitly or implicitly considers the thermodynamic limit. In that limit, one has

$$n_2(\vec{r}_1, \vec{r}_2) = \rho^2 g(\vec{r}_2 - \vec{r}_1), \quad (\text{III-18})$$

with  $g(\infty) = 1$ . [Compare, e.g., (III-5).] Notice that Hill in his book defines  $g$  by  $n_2 = \rho^2 g$  for finite  $N$ . In his case, then,  $g(\infty) = 1 + O(1/N)$ .

#### IV. SOME PROPERTIES OF THE PAIR DISTRIBUTION FUNCTION

In the previous chapter we have given the definition (with the canonical ensemble) of the molecular distribution functions. We will now derive some important properties of, in particular, the pair distribution  $n_2(\vec{r}_1, \vec{r}_2)$  [or of  $g(\vec{r})$ ]. The Hamiltonian, which in general was given by [cf. (II-1)]

$$H = \sum_i \frac{\vec{p}_i^2}{2m} + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N),$$

reduces, in the important case that the potential energy is a sum of pair interactions, to

$$H = \sum_i \frac{\vec{p}_i^2}{2m} + \sum_{i < k} \phi(\vec{r}_{ik}). \quad (\text{IV-1})$$

##### A. The Equations of State

The macroscopic energy of our systems (i.e., the average internal energy) is for the Hamiltonian (IV-1) given by

$$U = (N! h^{3N} Z_N)^{-1} \int e^{-\beta H} \left( \sum_i \frac{\vec{p}_i^2}{2m} + \sum_{i < k} \phi(\vec{r}_{ik}) \right) d\vec{r}_1 \dots d\vec{p}_N. \quad (\text{IV-2})$$

Performing the integrations over all momenta and over all but two coordinates  $\vec{r}_1$  and  $\vec{r}_2$ , we find, with (III-14),

$$U = (3/2) NkT + (1/2) \int_V n_2(\vec{r}_1, \vec{r}_2) \phi(\vec{r}_{12}) d\vec{r}_1 d\vec{r}_2. \quad (\text{IV-3})$$

This is called the caloric equation of state; it expresses  $U$  as a function of volume  $V$  and temperature  $T$ . In the thermodynamic limit, we can also write

$$u \equiv \frac{U}{N} = (3/2) kT + (1/2) \rho \int g(\vec{r}_{12}) \phi(\vec{r}_{12}) d\vec{r}_{12}, \quad (\text{IV-4})$$

or for an isotropic system,

$$u = (3/2) kT + 2\pi\rho \int_0^\infty g(r) \phi(r) r^2 dr. \quad (\text{IV-5})$$

Further, one can make use of the so-called virial theorem. This states that for a system in equilibrium, the virial of the external and internal forces exerted on the system is equal to minus twice the average kinetic energy of the system. The virial is defined by

$$\left\langle \sum_i \vec{r}_i \cdot \vec{F}_i \right\rangle = -3pV - \left\langle \sum_{i < k} \vec{r}_{ik} \cdot \frac{\partial \phi}{\partial \vec{r}_{ik}} \right\rangle, \quad (\text{IV-6})$$

where  $\vec{F}_i$  is the sum of external and internal forces on particle  $i$ ,  $V$  is the volume, and  $p$  is the pressure. We have, therefore,

$$pV = (2/3) \sum_i \frac{\langle \vec{p}_i^2 \rangle}{2m} - (1/3) \left\langle \sum_{i < k} \vec{r}_{ik} \cdot \frac{\partial \phi}{\partial \vec{r}_{ik}} \right\rangle, \quad (\text{IV-7})$$

or

$$pV = NkT - (1/3)(N!h^3N Z_N)^{-1} \int e^{-\beta H} \sum_{i < k} \vec{r}_{ik} \cdot \frac{\partial \phi}{\partial \vec{r}_{ik}} d\vec{r}_1 \dots d\vec{p}_N.$$

Performing the integrations as far as possible, we find

$$pV = NkT - (1/6) \int_V n_2(\vec{r}_1, \vec{r}_2) \vec{r}_{12} \cdot \frac{\partial \phi}{\partial \vec{r}_{12}} d\vec{r}_1 d\vec{r}_2. \quad (\text{IV-8})$$

This is the thermal equation of state; it expresses  $p$  as a function of volume and temperature. In the thermodynamic limit, we can write

$$pv = kT - (1/6) \rho \int g(\vec{r}_{12}) \vec{r}_{12} \cdot \frac{\partial \phi}{\partial \vec{r}_{12}} d\vec{r}_{12}, \quad (\text{IV-9})$$

where  $v = V/N$  is the volume per particle.

If the system is isotropic, then, because

$$\vec{r}_{12} \cdot \frac{\partial \phi}{\partial \vec{r}_{12}} = r_{12} \frac{d\phi}{dr_{12}},$$

we have

$$pv = kT - \frac{2\pi}{3} \rho \int_0^\infty g(r) \frac{d\phi}{dr} r^3 dr. \quad (\text{IV-10})$$

The important equations (IV-3) and (IV-8) can alternatively be derived from the expression (III-16) for the free energy, when we make use of the well-known thermodynamic relations

$$p = -\left(\frac{\partial F}{\partial V}\right)_T \text{ and } U = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V = \frac{\partial(\beta F)}{\partial\beta}. \quad (\text{IV-11})$$

Indeed,

$$U = -\frac{\partial \log Z_N}{\partial\beta} = \frac{1}{N! h^{3N} Z_N} \int H e^{-\beta H} d\vec{r}_1 \dots d\vec{p}_N, \quad (\text{IV-12})$$

which is identical with (IV-2) above.

The alternative derivation of the thermal equation of state is a little more difficult. We start from

$$p = kT \frac{\partial \log Z_N}{\partial V} = kT \frac{\partial \log Q_N}{\partial V} \quad (\text{cf. III-16}).$$

The difficulty now is that  $Q_N$  depends on volume through the limits of integration. Suppose the volume is a cube of edge  $L$ . Then we put (as was first done by H. S. Green)  $\vec{r}_j^1 = (1/L) \vec{r}_j$ . Then,

$$Q_N = \frac{1}{N!} \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_1 \dots d\vec{r}_N = \frac{L^{3N}}{N!} \int e^{-\beta V(\vec{r}_1^1, \dots, \vec{r}_N^1)} d\vec{r}_1^1 \dots d\vec{r}_N^1,$$

and

$$p = \frac{kT}{Q_N} \frac{\partial Q_N}{\partial V} = \frac{kT}{Q_N} \frac{1}{3L^2} \frac{\partial Q_N}{\partial L} = \frac{kT}{Q_N 3L^2 N!} \int (3NL^{3N-1} - \beta L^{3N} \frac{\partial V}{\partial L}) e^{-\beta V} d\vec{r}_1^1 \dots d\vec{r}_N^1.$$

Further,

$$\frac{\partial V(L\vec{r}_1^1, \dots, L\vec{r}_N^1)}{\partial L} = \sum_{i < k} \vec{r}_{ik}^1 \cdot \frac{\partial \phi(\vec{r}_{ik}^1)}{\partial \vec{r}_{ik}^1}.$$

Therefore,

$$pV = \frac{kTL}{3} \left( \int e^{-\beta V} d\vec{r}_1 \dots d\vec{r}_N \right)^{-1} \int \left( 3NL^{3N-1} - \beta L^{3N} \sum_{i < k} \vec{r}_{ik}^1 \cdot \frac{\partial \phi(\vec{r}_{ik}^1)}{\partial \vec{r}_{ik}^1} \right) e^{-\beta V} \frac{d\vec{r}_1 \dots d\vec{r}_N}{L^{3N}}.$$

or

$$pV = NkT - (1/3) \left\langle \sum_{i < k} \vec{r}_{ik} \cdot \frac{\partial \phi(\vec{r}_{ik})}{\partial \vec{r}_{ik}} \right\rangle, \quad (\text{IV-13})$$

which is identical to (IV-7).

The fact that the identification

$$F = -kT \log Z_N,$$

via the usual thermodynamic relations, leads to a form of the equations of state, which was also found directly, can to some extent be considered as a proof of this relation (cf., for the above derivations, Ref. 2).

#### B. The Function $g(\vec{r})$ as the Functional Derivative of the Free Energy

The equations of state discussed above are widely known. We will now derive an important property of  $g(r)$  which is much less known (cf. Refs. 1 and 7). We will show that, but for a factor  $(1/2)\rho$ ,  $g(r)$  is the functional derivative with respect to the pair potential of the free energy per particle.

According to our definitions, we have [cf. (III-12) and (III-14)]

$$Q_N = \frac{1}{N!} \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_1 \dots d\vec{r}_N,$$

and

$$n_2(\vec{r}_1, \vec{r}_2) = N(N-1) \left( \int e^{-\beta V} d\vec{r}_1 \dots d\vec{r}_N \right)^{-1} \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_3 \dots d\vec{r}_N.$$

Let

$$V(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i < j} \phi_{ij}(\vec{r}_{ij})$$

and let the two-particle potential  $\phi$  vary by a small amount  $\delta\phi$ . Then

$$\delta Q_N = -\frac{\beta}{N!} \int \sum_{i < j} \delta\phi_{ij} e^{-\beta \sum \phi_{ij}} d\vec{r}_1 \dots d\vec{r}_N.$$

As all terms in the sum are equal, one has

$$\begin{aligned}\delta Q_N &= -\beta \frac{N(N-1)}{2N!} \int \delta \phi_{12} d\vec{r}_1 d\vec{r}_2 \int e^{-\beta \sum \phi_{ij}} d\vec{r}_3 \dots d\vec{r}_N \\ &= -(\beta/2) Q_N \int \delta \phi_{12} n_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2,\end{aligned}$$

and

$$\delta \log Q_N = -(\beta/2) \int \delta \phi_{12} n_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = -(\beta/2) \rho^2 V \int \delta \phi(\vec{r}) g(\vec{r}) d\vec{r}.$$

Now if  $f(v, T)$  is the free energy per particle, we have

$$Nf = -kT \log Z_N = -kT \log Q_N - (3/2) NkT \log \frac{2\pi mkT}{h^2},$$

and

$$N\delta f = -kT \delta \log Q_N.$$

Hence,

$$\delta f = (1/2) \rho \int \delta \phi(\vec{r}) g(\vec{r}) d\vec{r}. \quad (\text{IV-14})$$

We shall see in the following that for  $f$  a cluster expansion can be given which is an expansion in powers of the density. The theorem (IV-14) will enable us to deduce from this expansion a similar expansion for the pair distribution  $g(r)$ .

#### Remark

Suppose that the variation of the total potential energy can be written as a sum of three-particle interactions,

$$\delta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i < j < k} \delta \phi_{ijk}(\vec{r}_i, \vec{r}_j, \vec{r}_k). \quad (\text{IV-15})$$



We then obtain in a similar way as above

$$\begin{aligned}\delta Q_N &= -\frac{\beta}{N!} \frac{N(N-1)(N-2)}{6} \int \delta \phi_{123} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_4 \dots d\vec{r}_N \\ &= -(\beta/6) Q_N \int \delta \phi_{123} n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3,\end{aligned}$$

and

$$\delta \log Q_N = -(\beta/6) \int \delta \phi_{123} n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3.$$

Or, if we define, in the thermodynamic limit,

$$n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \rho^3 g_3(\vec{r}_{12}, \vec{r}_{13}),$$

then,

$$\delta f = (1/6) \rho^2 \int \delta \phi_{123}(\vec{\rho}_1, \vec{\rho}_2) g_3(\vec{\rho}_1, \vec{\rho}_2) d\vec{\rho}_1 d\vec{\rho}_2; \quad (\text{IV-16})$$

i.e., also the three-particle, etc., distribution functions can in a certain sense be considered as functional derivatives of the free energy per particle.

### C. A System of Integral Equations for the Molecular Distribution Functions

#### 1. The Hierarchy

In the canonical ensemble, we defined (cf. Ch. III)

$$n_m(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_m) = \frac{N(N-1)\dots(N-m+1)}{N! Q_N} \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_{m+1} \dots d\vec{r}_N. \quad (\text{IV-17})$$

Let  $V$  be a sum of pair potentials:

$$V(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i < j} \phi_{ij}(\vec{r}_{ij}).$$

Then, on differentiating (IV-17) with respect to  $\vec{r}_1$ , we obtain

$$\begin{aligned}
 \frac{1}{\beta} \frac{\partial n_m}{\partial \vec{r}_1} &= - \frac{1}{(N-m)! Q_N} \int \sum_{j=2}^N \frac{\partial \phi_{1j}}{\partial \vec{r}_1} e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_{m+1} \dots d\vec{r}_N \\
 &= - \sum_{j=2}^m \frac{\partial \phi_{1j}}{\partial \vec{r}_1} n_m(\vec{r}_1, \dots, \vec{r}_m) - \frac{1}{(N-m)! Q_N} \int \sum_{k=m+1}^N \frac{\partial \phi_{1k}}{\partial \vec{r}_1} e^{-\beta V} d\vec{r}_{m+1} \dots d\vec{r}_N \\
 &= - \sum_{j=2}^m \frac{\partial \phi_{1j}}{\partial \vec{r}_1} n_m(\vec{r}_1, \dots, \vec{r}_m) - \int \frac{\partial \phi_{1,m+1}}{\partial \vec{r}_1} n_{m+1}(\vec{r}_1, \dots, \vec{r}_{m+1}) d\vec{r}_{m+1}.
 \end{aligned} \tag{IV-18}$$

We have here a set of linear integro-differential equations connecting two successive configurational distribution functions. These equations are a particular case of very general relations, which, also for nonstationary ensembles, connect the time-dependent distribution functions in phase space  $P_m$  and  $P_{m+1}$ . They can be derived from the Liouville equation by integration. (For their derivation, see some of the general references.) They are often called the Bogolyubov-Born-Green-Yvon-Kirkwood (BBGYK) hierarchy.

In our special case of the canonical ensemble, we have, for  $m = 2$ ,

$$\frac{1}{\beta} \frac{\partial n_2(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} = -n_2(\vec{r}_1, \vec{r}_2) \frac{\partial \phi_{12}}{\partial \vec{r}_1} - \int \frac{\partial \phi_{13}}{\partial \vec{r}_1} n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) d\vec{r}_3 \tag{IV-19}$$

or also

$$\frac{1}{\beta} \frac{\partial \log n_2(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} = - \frac{\partial \phi_{12}}{\partial \vec{r}_1} - \int \frac{\partial \phi_{13}}{\partial \vec{r}_1} \frac{n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)}{n_2(\vec{r}_1, \vec{r}_2)} d\vec{r}_3. \tag{IV-20}$$

This equation was presumably first derived by Yvon. In Fisher's book, (IV-18) is called the Bogolyubov equation, and it is discussed there in great detail; e.g., it is solved there by means of a series expansion in the density  $\rho$ .

The equation (IV-20) is immediately related to the so-called potential of mean force. The mean force on particle 1, when the position of 2 is given and one averages over the positions of all other particles, is clearly

$$\vec{F}_1(\vec{r}_1, \vec{r}_2) = \frac{\int - \frac{\partial V}{\partial \vec{r}_1} e^{-\beta V} d\vec{r}_3 \dots d\vec{r}_N}{\int e^{-\beta V} d\vec{r}_3 \dots d\vec{r}_N} = \frac{1}{\beta} \frac{\partial \log n_2(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1}. \tag{IV-21}$$

This is just the left-hand side of (IV-20). The first term on the right-hand side is the direct contribution of particle 2; the second term is the average contribution from particles 3,4,...,N. The potential of mean force  $W_2(\vec{r}_1, \vec{r}_2)$  should obey

$$-\frac{\partial W_2(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} = \vec{F}_1(\vec{r}_1, \vec{r}_2). \quad (\text{IV-22})$$

In view of (IV-21), we have

$$\log n_2(\vec{r}_1, \vec{r}_2) = -\beta W_2(\vec{r}_1, \vec{r}_2) + \text{constant},$$

or

$$n_2(\vec{r}_1, \vec{r}_2) = \text{constant} \cdot e^{-\beta W_2(\vec{r}_1, \vec{r}_2)} \quad (\text{IV-23})$$

More specifically,  $W_2(\vec{r}_1, \vec{r}_2)$  is usually defined by

$$e^{-\beta W_2(\vec{r}_1, \vec{r}_2)} = \frac{1}{(N-2)! Q_N} \int e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)} d\vec{r}_3 \dots d\vec{r}_N. \quad (\text{IV-24})$$

If molecules 3,...,N had no interaction with molecules 1 and 2, this would reduce to  $e^{-\beta \phi_{12}}$ . The constant in (IV-23) is then seen to be given by

$$\frac{Q_{N-2}}{Q_N} = z^2,$$

where  $z$  is called the activity (see later chapters). In an analogous way, as  $W_2$ , one can introduce  $W_3$ , etc., but we will not need them here.

Kirkwood has discussed an integral equation which is slightly different from (IV-20). He introduces

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \xi) = \xi \sum_{j=2}^N \phi_{ij}(\vec{r}_{ij}) + \sum_{j=2}^N \sum_{k=j+1}^N \phi_{jk}(\vec{r}_{jk}), \quad (\text{IV-25})$$

where particle 1 is coupled to the others by means of a coupling parameter  $\xi$ , which may have values from 0 to 1.

If this potential is introduced into the definition of  $n_2(\vec{r}_1, \vec{r}_2)$ , one obtains, by differentiating with respect to  $\xi$ ,

$$\frac{1}{\beta} \frac{\partial \log n_2(\vec{r}_1, \vec{r}_2, \xi)}{\partial \xi} = -\phi_{12} - \int \phi_{13}(\vec{r}_{13}) \left\{ \frac{n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3, \xi)}{n_2(\vec{r}_1, \vec{r}_2, \xi)} - \frac{n_2(\vec{r}_1, \vec{r}_3, \xi)}{\rho} \right\} d\vec{r}_3. \quad (\text{IV-26})$$

## 2. The Superposition Approximation

Let us remember that  $n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)/n_2(\vec{r}_1, \vec{r}_2)$  is proportional to the probability of finding a particle at  $\vec{r}_3$  once you know that two molecules are at  $\vec{r}_1$  and  $\vec{r}_2$ , respectively. To find an equation for  $n_2$  alone (without higher distribution functions), Kirkwood first introduced the assumption that

$$\frac{n_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)}{n_2(\vec{r}_1, \vec{r}_2)} = \frac{n_2(\vec{r}_1, \vec{r}_3) n_2(\vec{r}_2, \vec{r}_3)}{\rho^3}, \quad (\text{IV-27})$$

or the probability of finding a third particle at  $\vec{r}_3$ , when given that two particles are at  $\vec{r}_1$ , and  $\vec{r}_2$  is put equal to the probability of finding particle 3 at  $\vec{r}_3$  when you know that particle 1 is at  $\vec{r}_1$ , times the probability of finding particle 3 at  $\vec{r}_3$  when you know that particle 2 is at  $\vec{r}_2$ . This assumption, which obviously is valid at low densities, is called the superposition approximation. We shall see later that, at higher densities, it begins to fail.

In the literature, one often meets with the superposition approximation in a different, though equivalent, form; e.g., in terms of the g-functions (thermodynamic limit), it reads

$$g_3(1,2,3) = g_2(1,2) g_2(1,3) g_2(2,3). \quad (\text{IV-28})$$

In terms of potentials of mean force,

$$W_3(1,2,3) = W_2(1,2) + W_2(1,3) + W_2(2,3), \quad (\text{IV-29})$$

and in terms of the specific distribution functions in configuration space, it can be written

$$\frac{\rho_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)}{\rho_1(\vec{r}_1) \rho_1(\vec{r}_2) \rho_1(\vec{r}_3)} = \frac{\rho_2(\vec{r}_1, \vec{r}_2)}{\rho_1(\vec{r}_1) \rho_1(\vec{r}_2)} \cdot \frac{\rho_2(\vec{r}_1, \vec{r}_3)}{\rho_1(\vec{r}_1) \rho_1(\vec{r}_3)} \cdot \frac{\rho_2(\vec{r}_2, \vec{r}_3)}{\rho_1(\vec{r}_2) \rho_1(\vec{r}_3)}. \quad (\text{IV-30})$$

Except for terms of order  $N^{-2}$ , it is equivalent to (IV-27). If (IV-27) is substituted in (IV-20), one obtains the approximate equation

$$\frac{1}{\beta} \frac{\partial \log n_2(\vec{r}_1, \vec{r}_2)}{\partial \vec{r}_1} = - \frac{\partial \phi_{12}}{\partial \vec{r}_1} - \frac{1}{\rho^3} \int \frac{\partial \phi_{13}}{\partial \vec{r}_1} n_2(\vec{r}_1, \vec{r}_3) n_2(\vec{r}_2, \vec{r}_3) d\vec{r}_3. \quad (\text{IV-31})$$

This equation, in which  $n_2$  is the only unknown function, is generally called the Born-Green equation. It is widely used to obtain approximate pair distribution functions.

If (IV-27) is assumed for every  $\xi$  and substituted in (IV-26), one obtains

$$\frac{1}{\beta} \frac{\partial \log n_2(\vec{r}_1, \vec{r}_2, \xi)}{\partial \xi} = -\phi_{12} - \frac{1}{\rho^3} \int \phi_{13} \left\{ n_2(\vec{r}_1, \vec{r}_3, \xi) n_2(\vec{r}_2, \vec{r}_3, \xi) - \rho^2 n_2(\vec{r}_1, \vec{r}_3, \xi) \right\} d\vec{r}_3. \quad (\text{IV-32})$$

This is the Kirkwood integral equation for the pair distribution function. Whereas (IV-20) and (IV-26) are exact, (IV-31) and (IV-32) are only approximate. One can expand both the exact and the approximate  $n_2$  functions in a power series in the density  $\rho$ . We shall see that the term in  $\rho^2$  in the approximate (Born-Green or Kirkwood)  $n_2$  function begins to deviate. It is hard to know just how good the approximate  $n_2$  function is at higher (e.g., liquid) densities.

One might as well have started from the next higher equation in the hierarchy (IV-18), the one relating  $n_3$  and  $n_4$ . One can then make for  $n_4$  an assumption analogous to the superposition assumption (IV-27). This probably gives an improvement compared with the above procedure.

#### D. The Fluctuation Integral: $\frac{1 + \rho \int \{g(\vec{r}) - 1\} d\vec{r}}$

In Ch. I, we mentioned the relation

$$1 + \rho \int \{g(\vec{r}) - 1\} d\vec{r} = \frac{\langle n_\Omega^2 \rangle - \langle n_\Omega \rangle^2}{\langle n_\Omega \rangle} \quad (\text{IV-33})$$

[cf. (I-4)], where  $n_\Omega$  is the number of particles in an arbitrary volume  $\Omega$ , which, however, should be small compared to the total volume of our system, but still large compared to the correlation length, i.e., the distance for which  $g(r) - 1$  has become zero essentially. In a similar way, one can express

$$\frac{\langle n_\Omega^3 \rangle - \langle n_\Omega \rangle^3}{\langle n_\Omega \rangle^2}$$

in terms of an integral of  $g_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)$ . This type of integral is sometimes called a fluctuation integral. We will prove (IV-33) now. We have

$$n_\Omega = \sum_{i=1}^N \int_\Omega \delta(\vec{r} - \vec{r}_i) d\vec{r}.$$

From our definition (III-15), we see that

$$\begin{aligned}
n_1(\vec{r}) &= N \left\{ \int e^{-\beta V} d\vec{r}_1 \dots d\vec{r}_N \right\}^{-1} \int e^{-\beta V(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)} d\vec{r}_2 \dots d\vec{r}_N \\
&= N \left\{ \int e^{-\beta V} d\vec{r}_1 \dots d\vec{r}_N \right\}^{-1} \int e^{-\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)} \delta(\vec{r} - \vec{r}_1) d\vec{r}_1 \dots d\vec{r}_N \\
&= \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i) \right\rangle.
\end{aligned}$$

Hence,

$$\langle n_\Omega \rangle = \int_\Omega n_1(\vec{r}) d\vec{r}. \quad (\text{IV-34})$$

Similarly

$$\begin{aligned}
n_\Omega^2 &= \sum_{i=1}^N \sum_{j=1}^N \int_\Omega \int_\Omega \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) d\vec{r} d\vec{r}' \\
&= \sum_{i=1}^N \int_\Omega \delta(\vec{r} - \vec{r}_i) d\vec{r} + \sum_{i \neq j}^N \int_\Omega \int_\Omega \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) d\vec{r} d\vec{r}'.
\end{aligned}$$

Again, from our definition (III-14), it is easily verified that

$$n_2(\vec{r}, \vec{r}') = \left\langle \sum_{i=1, i \neq j}^N \sum_{j=1}^N \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle, \quad (\text{IV-35})$$

and therefore

$$\langle n_\Omega^2 \rangle = \langle n_\Omega \rangle + \int_\Omega \int_\Omega n_2(\vec{r}, \vec{r}') d\vec{r} d\vec{r}',$$

or

$$\langle n_\Omega^2 \rangle - \langle n_\Omega \rangle^2 = \langle n_\Omega \rangle + \int_\Omega \int_\Omega \left\{ n_2(\vec{r}, \vec{r}') - n_1(\vec{r}) n_1(\vec{r}') \right\} d\vec{r} d\vec{r}'.$$



Hence,

$$\frac{\langle n_{\Omega}^2 \rangle - \langle n_{\Omega} \rangle^2}{\langle n_{\Omega} \rangle} = 1 + \rho \int_{\Omega} \left\{ \frac{n_2(\vec{r}_{12})}{\rho^2} - 1 \right\} d\vec{r}_{12}, \quad (\text{IV-36})$$

or in the thermodynamic limit

$$\frac{\langle n_{\Omega}^2 \rangle - \langle n_{\Omega} \rangle^2}{\langle n_{\Omega} \rangle} = 1 + \rho \int \left\{ g(\vec{r}) - 1 \right\} d\vec{r}, \quad (\text{IV-37})$$

where now the integral must be extended to infinity.

### Remark

If in (IV-36),  $\Omega$  were taken to be  $V$  (total volume), we would have got

$$1 + \rho \int_V \left\{ \frac{n_2(\vec{r}_1, \vec{r}_2)}{\rho^2} - 1 \right\} d\vec{r}_2 = 0. \quad (\text{IV-38})$$

From (III-7), one easily verifies that this relation is indeed exact. On comparing (IV-37) and (IV-38), one realizes that one ought to be careful in replacing  $n_2(\vec{r}_1, \vec{r}_2)$  by  $\rho^2 g(\vec{r}_{12})$ . As remarked before, these quantities are equal except for terms of order  $N^{-1}$ .\* When integrating over the total volume  $V$ , these terms would become important. As long as  $\Omega \ll V$ , these terms can be neglected in the integration over volume  $\Omega$ , and for such volumes  $\Omega$ , (IV-37) is valid.

E. The Integral: 
$$\int \frac{g(\vec{r}) - 1}{\pi r^2} d\vec{r}$$

This integral, which should not be confused with that occurring in (IV-37), plays a remarkable role in the static approximation of scattering

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\*For the ideal gas, for example,

$$n_2(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{V^2};$$

hence,

$$\frac{n_2(\vec{r}_1, \vec{r}_2)}{\rho^2} = 1 - \frac{1}{N},$$

which approaches 1 for large separation only when terms of order  $N^{-1}$  are neglected.

(cf. Introduction). For the content of this section, see G. Placzek, B. R. A. Nijboer, and L. Van Hove, Phys. Rev. 82, 392 (1951). In the static theory of scattering, we derived the formula of Zernike and Prins [cf. (I-2)]:

$$\sigma(\vec{\kappa}) = 1 + \rho \int \left\{ g(\vec{r}) - 1 \right\} e^{i\vec{\kappa} \cdot \vec{r}} d\vec{r} \quad (\text{IV-39})$$

Here,  $\vec{\kappa} = \vec{k}_0 - \vec{k}$ ,  $\rho$  is the density, and the cross section is expressed in units of the cross section of an isolated particle. For convenience, let us introduce as unit of length the cube root of the volume per particle; then,  $\rho = 1$ . Further, we introduce  $\vec{\kappa} = 2\pi \vec{h}$ .

Then (IV-39) simplifies to

$$\sigma(\vec{h}) - 1 = \int \left\{ g(\vec{r}) - 1 \right\} e^{2\pi i \vec{h} \cdot \vec{r}} d\vec{r}. \quad (\text{IV-40})$$

Suppose we now want to find the total scattering cross section for a randomly oriented system (e.g., a polycrystal or a liquid). We must then integrate over all angles and at the same time average over all directions of  $\vec{h}$ . It is convenient to combine these two operations. If we express the total cross section in units of the total cross section of an isolated particle, we have

$$\sigma_{\text{tot}} = \int_{-1}^{+1} (1/2) d(\cos \theta) \int \sigma(\vec{h}) \frac{d\Omega_h}{4\pi},$$

where  $d\Omega_h$  is an element of solid angle in  $\vec{h}$ -space. Because

$$h = (2/\lambda) \sin \frac{\theta}{2} = \frac{\{2(1 - \cos \theta)\}^{1/2}}{\lambda},$$

$$d(\cos \theta) = -\lambda^2 h dh,$$

and hence

$$\sigma_{\text{tot}} = \frac{\lambda^2}{8\pi} \int_0^{2/\lambda} h dh \int \sigma(\vec{h}) d\Omega_h = \frac{\lambda^2}{8\pi} \int_S \sigma(\vec{h}) \frac{d\vec{h}}{h},$$

where the integration has to be extended over a sphere of radius  $2/\lambda$ .

One can also write

$$\sigma_{\text{tot}} = 1 - \frac{\lambda^2}{8\pi} \int_S \frac{1 - \sigma(\vec{h})}{h} d\vec{h}. \quad (\text{IV-41})$$

For large  $h$  (i.e.,  $\lambda/[2 \sin(\theta/2)] \ll$  atomic distances), interference effects become negligible and  $\sigma(\vec{h})$  tends to 1. As a consequence, for short wavelength of the incoming radiation, the integration in (IV-41) may be extended over the whole of  $\vec{h}$ -space.

We have then, for this asymptotic value,

$$\sigma_{\text{tot,as}} = 1 - \frac{\lambda^2}{8\pi} I, \quad (\text{IV-42})$$

where

$$I = \int \frac{1 - \sigma(\vec{h})}{h} d\vec{h} = \int \frac{1 - g(\vec{r})}{\pi r^2} d\vec{r}. \quad (\text{IV-43})$$

The latter equality follows from (IV-40) and Parseval's theorem and by noting that  $1/h$  is the Fourier transform of  $1/(\pi r^2)$ . The problem was to evaluate  $I$  for dense systems as crystals and liquids. For an ideal rigid lattice,  $g(r)$  is just a sum of  $\delta$ -functions, and the integral (IV-43) reduces to a lattice sum, which unfortunately converges extremely slowly. It is hard to estimate  $I$  from (IV-43). However, one may apply the following procedure:

$$I = \int \left\{ 1 - g(\vec{r}) \right\} \frac{e^{-\pi r^2}}{\pi r^2} d\vec{r} + \int \left\{ 1 - g(\vec{r}) \right\} \frac{(1 - e^{-\pi r^2})}{\pi r^2} d\vec{r}.$$

By applying Parseval's theorem again for the second integral, we find

$$I = \int \left\{ 1 - g(\vec{r}) \right\} \frac{e^{-\pi r^2}}{\pi r^2} d\vec{r} + \int \left\{ 1 - \sigma(\vec{h}) \right\} \frac{\Phi(\sqrt{\pi} h)}{h} d\vec{h},$$

where

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$$

is the so-called error function. Now

$$\int \frac{e^{-\pi r^2}}{\pi r^2} d\vec{r} = 2,$$

and

$$\int \frac{\Phi(\sqrt{\pi h})}{h} d\vec{h} = 1;$$

hence,

$$I = 3 - \int g(\vec{r}) \frac{e^{-\pi r^2}}{\pi r^2} d\vec{r} - \int \sigma(\vec{h}) \frac{\Phi(\sqrt{\pi h})}{h} d\vec{h}. \quad (\text{IV-44})$$

The factors  $e^{-\pi r^2}/(\pi r^2)$  and  $\Phi(\sqrt{\pi h})/h$  make both integrals converge very rapidly.

We see that three is an upper bound for the integral  $I$ , and for dense systems one may expect the deviation from three to be small. The reason is that  $g(0) = 0$ , and for values of  $\vec{r}$  where  $g(\vec{r})$  becomes appreciable, the second factor in the first integral has already become very small. Something similar holds for the second integral:

$$\sigma(0) = 1 + \int \{g(\vec{r}) - 1\} d\vec{r} = \chi_T,$$

i.e., the relative isothermal compressibility, which for dense systems is only a few thousandths.

From (IV-44) it is easy to compute  $I$  for a rigid lattice. Some results are compiled in the following table [ $S$  is the first integral in (IV-44),  $R$  the second]:

	<u>S</u>	<u>R</u>	<u>I</u>
fcc	0.058191	0.053347	2.888462
hcp	0.058193	0.053340	2.888377
bcc	0.059068	0.053650	2.888282
Simple cubic	0.086169	0.076533	2.837298
Diamond	0.164718	0.141882	2.693400

These results indicate that a more open structure leads to smaller value of  $I$ . In the paper quoted on page 32,  $I$  was also evaluated for harmonically vibrating lattices. If we put

$$I = I_0 - I_d, \quad (\text{IV-45})$$

where  $I_0$  is the value pertaining to the rigid lattice, it is found that  $I_d$  is essentially positive and is given by

$$I_d = \beta \chi_T, \quad (\text{IV-46})$$

where  $\beta$  is a numerical factor  $\approx 1.5$ , and  $\chi_T$  is the relative isothermal compressibility  $\approx 0.003$  at room temperature.

For liquids, (IV-44) makes it possible to estimate  $I$  with an accuracy of about 5%.

An intriguing question is what is the maximum value that  $I$  can have. It seems rather plausible that the maximum value is reached for the fcc structure, but as far as I know no proof has yet been given.

It will be obvious that the question for which structure the integral

$$K = \int \frac{g(\vec{r}) - 1}{r} d\vec{r} \quad (\text{IV-47})$$

has a minimum, is closely related to the question posed above and that the answer will be just the reciprocal structure to the solution of the first problem. One would then surmise that  $K$  would be a minimum for the rigid bcc lattice (which is reciprocal to the fcc lattice). Now  $K$  has a simple physical significance. It represents the energy (per particle) of a system of negative point charges in a neutralizing positive background, if we consider the electrostatic energy only. Indeed, it is generally assumed that for a low-density electron gas, a bcc structure would have minimum energy (Wigner, Fuchs). The energy value itself follows immediately from the data in our table on page 34.

## V. THE ONE-DIMENSIONAL SYSTEM

We will now briefly consider the application of our formulas to a one-dimensional system. (Cf. Gürsey, Proc. Cambr. Phil. Soc. 46, 182 (1950); Van Hove, Physica 16, 137 (1950); and the book of Münster, mentioned in the Introduction.)

Let us first try to evaluate

$$Q_N = \frac{1}{N!} \int e^{-\beta V(x_1, x_2, \dots, x_N)} dx_1 dx_2 \dots dx_N.$$

Let us suppose that the potential energy  $V$  is a sum of terms between nearest neighbors only; i.e.,

$$V(x_1, \dots, x_N) = \sum_i \phi(x_{i+1} - x_i). \quad (V-1)$$

Let us take

$$0 = x_0 < x_1 < x_2 < \dots < x_N < x_{N+1} = L. \quad (V-2)$$

That is, we take  $x_0$  and  $x_{N+1}$  fixed at the ends of our "volume"  $L$ , and the order of the other particles is given. Then,

$$\begin{aligned} Q_N(L) &= \frac{1}{N!} \int_0^L dx_N \int_0^L dx_{N-1} \dots \int_0^L dx_1 e^{-\beta \sum_{i=0}^N \phi(x_{i+1} - x_i)} \\ &= \int_0^L dx_N \int_0^{x_N} dx_{N-1} \dots \int_0^{x_2} dx_1 e^{-\beta \sum_{i=0}^N \phi(x_{i+1} - x_i)} \\ &= \int_0^L dx_N e^{-\beta \phi(L - x_N)} \int_0^{x_N} dx_{N-1} e^{-\beta \phi(x_N - x_{N-1})} \dots \\ &\quad \int_0^{x_2} dx_1 e^{-\beta \phi(x_2 - x_1) - \beta \phi(x_1)}. \end{aligned} \quad (V-3)$$

Now take the Laplace transform of  $Q_N(L)$ , which is an  $(N+1)$ -fold convolution product:



$$\tilde{Q}_N(s) \equiv \int_0^\infty e^{-sL} Q_N(L) = \{\tilde{\Phi}(s)\}^{N+1},$$

where

$$\tilde{\Phi}(s) = \int_0^\infty e^{-sx - \beta \phi(x)} dx. \quad (V-4)$$

By applying the inversion formula of Laplace transformation and evaluating the resulting integral, e.g., by the theorem of residues, one obtains  $Q_N(L)$ . Let us first consider the simple case of one-dimensional hard spheres (rods) with length  $a$ . In this case,

$$\tilde{\Phi}(s) = \int_a^\infty e^{-sx} dx = \frac{e^{-sa}}{s}. \quad (V-5)$$

We then have

$$\begin{aligned} Q_N(L) &= \frac{1}{N!} \{L - (N+1)a\}^N, & L > (N+1)a; \\ &= 0 & L < (N+1)a. \end{aligned} \quad (V-6)$$

From

$$F = -kT \log Z_N = -kT \log \left( \frac{2\pi mkT}{h^2} \right)^{N/2} - kT \log Q_N,$$

we then find

$$P = - \left( \frac{\partial F}{\partial L} \right)_T = \frac{NkT}{L - (N+1)a}. \quad (V-7)$$

Introducing the average length per particle  $\ell = L/(N+1)$ , and neglecting 1 compared to  $N$ , we obtain

$$P(\ell - a) = kT. \quad (V-8)$$

This is the well-known equation of state for one-dimensional hard spheres, which was first obtained by Tonks in 1936.

#### Remark

One may easily verify that this equation of state can alternatively be derived from the virial equation in one dimension,

$$pL = NkT - (1/2)L\rho^2 \int_{-\infty}^{+\infty} g(x) x \frac{d\phi}{dx} dx, \quad (V-9)$$

by substituting the pair distribution function  $g(x)$  for one-dimensional rigid spheres as derived in Ch. I. Notice, however, that the average length per particle  $\ell$  was called there  $\ell + a$ .

In the more general case of an arbitrary two-particle interaction (but still restricting ourselves to nearest-neighbor interaction only), we have

$$Q_N(L) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{sL} \{\tilde{\Phi}(s)\}^{N+1} ds, \quad (V-10)$$

where  $c$  is chosen so that it is positive, and the path of integration lies to the right of all poles of  $\tilde{\Phi}(s)$ . One may then close the path of integration by an infinitely large circle enclosing the left-hand portion of the complex  $s$ -plane and evaluate  $Q_N(L)$  by the theorem of residues. Alternatively, in the thermodynamic limit  $N \rightarrow \infty$ ,  $L \rightarrow \infty$ ,  $\ell = L/(N+1)$  finite, one can evaluate  $\log Q_N(L)$  by the method of steepest descent. We have, for the integrand in (V-10),

$$e^{sL} \{\tilde{\Phi}(s)\}^{N+1} = \{e^{s\ell} \tilde{\Phi}(s)\}^{N+1} = e^{(N+1)\chi(s)}, \quad (V-11)$$

where

$$\chi(s) = s\ell + \log \tilde{\Phi}(s). \quad (V-12)$$

The first factor,  $e^{sL}$  increases with  $s$  very strongly, while the second factor,

$$\{\tilde{\Phi}(s)\}^{N+1},$$

decreases with  $s$  very strongly.

The saddle point  $s_0$  of the integrand of (V-10) is given by

$$\chi'(s_0) = \ell + \left( \frac{d}{ds} \log \tilde{\Phi}(s) \right)_{s=s_0} = 0. \quad (V-13)$$

By expanding  $\chi(s)$  around  $s_0$  and performing the integration, one finds

$$\lim_{N \rightarrow \infty} \{Q_N(L)\}^{\frac{1}{N+1}} = e^{s_0 \ell} \tilde{\Phi}(s_0),$$

or

$$\lim_{N \rightarrow \infty} \log Q_N(L) = s_0 L + (N+1) \log \tilde{\Phi}(s_0). \quad (V-14)$$

We now see that the pressure  $p$  is given by

$$p = kT \frac{\partial \log Q_N(L)}{\partial L} = kT \left\{ s_0 + (N+1) \left[ \ell + \frac{d}{ds_0} \log \tilde{\Phi}(s_0) \right] \frac{ds_0}{dL} \right\} = kT s_0, \quad (V-15)$$

by virtue of (V-13), so that in the thermodynamic limit,

$$Q_N(L) = e^{pL/kT} \left\{ \tilde{\Phi}\left(\frac{p}{kT}\right) \right\}^{N+1}, \quad (V-16)$$

and (V-13) becomes the equation of state,

$$\ell + kT \frac{\partial}{\partial p} \log \tilde{\Phi}\left(\frac{p}{kT}\right) = 0, \quad (V-17)$$

where  $\tilde{\Phi}$  was given by (V-4).

One can show that for  $0 < T < \infty$ ,

$$0 < - \left( \frac{\partial p}{\partial \ell} \right)_T < \infty; \quad (V-18)$$

i.e., the pressure decreases monotonically with increasing volume per particle. For  $T \rightarrow \infty$ , one finds that  $p \rightarrow kT/\ell$ ; and for  $T = 0$  (if the interaction has the usual form with a minimum at  $x_m$ ), one finds

$$\begin{aligned} p &= -\phi'(\ell), & \ell < x_m; \\ &= 0, & \ell > x_m. \end{aligned} \quad (V-19)$$

### Remarks

1. Gürsey has evaluated the isotherms for a potential consisting of a hard core + a rectangular attraction well (cf. his paper).

2. Van Hove has generalized (V-18). He shows that it holds in the one-dimensional case for an arbitrarily large but finite range of the force, without restricting himself to nearest-neighbor interaction only. This shows that a one-dimensional fluid has no phase transition.

In a similar way as the configuration integral, one can compute the distribution functions, in particular the pair distribution function, for a one-dimensional system with nearest-neighbor interactions only.

Let us consider again for a moment the situation described by (V-2). According to the canonical ensemble probability, the probability to find  $N$  particles at  $x_1, x_2, \dots, x_N$  is

$$n_N(x_1, \dots, x_N) = Q_N^{-1} \exp \{ -\beta [\phi(x_1) + \phi(x_2 - x_1) + \dots + \phi(L - x_N)] \}. \quad (\text{V-20})$$

To find the probability that the  $k^{\text{th}}$  particle is at  $x$ , one has to integrate this expression over all coordinates except  $x_k = x$ . Fixing the position of the  $k^{\text{th}}$  particle at  $x$  divides the system in two parts, one with length  $x$  and  $k - 1$  particles, and the other with length  $L - x$  and  $N - k$  particles.

One finds in this way,

$$\rho g(x) = \sum_k \frac{Q_{k-1}(x) Q_{N-k}(L-x)}{Q_N(L)}. \quad (\text{V-21})$$

Let us again take the case of hard rods. Using now (V-6) and going to the limit  $N \rightarrow \infty$ ,  $L \rightarrow \infty$ , one is led back to the result of Zernike and Prins, derived in Ch. I.

#### Remark

In the case of one dimension and nearest-neighbor interaction, it is rather obvious that the superposition approximation in the form  $g_3(1, 2, 3) = g_2(1, 2) g_2(2, 3)$  is strictly valid. As a result, the Born-Green equation is also rigorously valid in this case.

## VI. THE MAYER CLUSTER EXPANSIONS

### A. The Mayer Equations

I propose to spend the remaining time available for these lectures on the Mayer cluster expansion and some related topics. Here we have, so to speak, the prototype of modern many-body theory and the method of diagrams. This many-body theory has in the last 10 years or so shown a tremendous development, mainly in the treatment of interacting quantum systems. The inspiration has largely come from field theory and the method of Feynman graphs. However, some of the methods and considerations can be traced back to the Mayer cluster expansion (e.g., the reduction to connected diagrams). And, of course, if, e.g., in the Lee-Yang theory of interacting quantum particles, one goes to the limit  $\hbar \rightarrow 0$ , one is led back to the Mayer theory, and the graphs of Lee and Yang reduce to the Mayer graphs. We shall try to give a modern account of Mayer's theory, in which the connection with recent theories comes out a little more clearly than in the original treatment.

The configuration integral  $Q_N$  is given by

$$Q_N = \frac{1}{N!} \int e^{-\beta V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)} d\vec{r}_1 d\vec{r}_2 \dots d\vec{r}_N. \quad (\text{VI-1})$$

We shall usually (though not always) suppose that the potential energy is a sum of two-particle interactions

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i < k} \phi(\vec{r}_{ik}). \quad (\text{VI-2})$$

The molecular distribution functions are given by integrals similar to (VI-1). Once we know  $Q_N$ , we can compute all thermodynamic quantities. In particular, the equation of state is given by

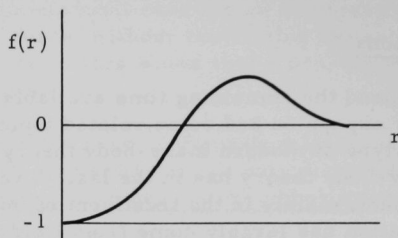
$$p = kT \frac{\partial \log Q_N}{\partial V}. \quad (\text{VI-3})$$

However, calculating these multidimensional integrals is difficult. J. Mayer (1937) succeeded in expanding  $\log Q_N$  in a power series in the density. From there, one is led immediately to the so-called virial expansion of the equation of state. We shall not touch upon the difficult problems related to the convergence of these expansions and to condensation.

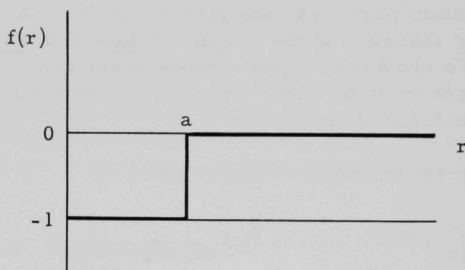
Instead of  $\phi(r)$ , which goes to infinity at short range, Mayer introduces the function

$$f_{ij}(r_{ij}) = e^{-\beta \phi(r_{ij})} - 1. \quad (\text{VI-4})$$

The general form of  $f(r)$  looks like



For hard spheres,  $f(r)$  looks like



where  $a$  is the diameter of the spheres. Now  $Q_N$  can be expanded in a sum of integrals over products of  $f$ 's:

$$Q_N = \frac{1}{N!} \int \prod_{i < j} (1 + f_{ij}) d\vec{r}_1 \dots d\vec{r}_N$$

$$= \frac{1}{N!} \int \left( 1 + \sum_{i < j} f_{ij} + \frac{1}{2!} \sum_{\substack{i < j \\ \text{no equal} \\ \text{pairs}}} \sum_{k < l} f_{ij} f_{kl} + \frac{1}{3!} \sum_{\substack{i < j \\ \text{no equal} \\ \text{pairs}}} \sum_{k < l} \sum_{m < n} f_{ij} f_{kl} f_{mn} + \dots \right) d\vec{r}_1 \dots d\vec{r}_N$$

(VI-5)

Each term can be represented by a graph, e.g.,

$$\prod_{i < j}^4 (1 + f_{ij}) = \begin{array}{cccccc} \cdot & \cdot & + & \vdots & + & \vdots & + & \vdots & + & \vdots & + & \vdots \\ (1) & (6) & (3) & (12) & (4) & & & & & & & \end{array}$$

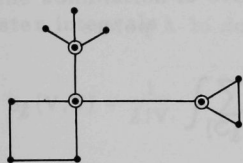
$$+ \begin{array}{cccccc} \vdots & + & \vdots & + & \vdots & + & \vdots & + & \vdots & + & \vdots \\ (12) & (4) & (12) & (3) & (6) & (1) & & & & & \end{array}$$

(VI-6)

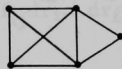


Each of the four points is represented by a dot. A line connecting  $i$  and  $j$  represents a factor  $f_{ij}$ . The numbers in parentheses give the number of terms represented by each graph when one labels the four points.

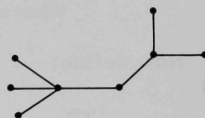
One will understand that in this theory the concepts of linear graph theory (i.e., points and lines between pairs of points) will play an important role. Let us mention a few definitions. A simple graph is a graph in which two points are connected by at most one line. A connected graph is one in which there is at least one path between any two points. An articulation point is a point where a graph can be cut into two or more disconnected parts. A graph without articulation points is called a star. A general connected graph is built from stars hanging together in the articulation points. If the stars are just single lines, one calls the graph a Cayley tree. If the stars are polygons, the graph is called a Husimi tree. For example:



Connected graph with articulation points ●



Star



Cayley tree

Let us return now to the expansion (VI-5). If we take the first term 1 only, then  $Q_N = V^N/N!$ , and  $p = NkT/V$ ; i.e., one obtains the ideal gas law. If one restricts oneself to so-called simultaneous two-particle collisions, i.e., if one includes terms like  $f_{12}f_{34}f_{67}$  but excludes terms like  $f_{12}f_{13}$  (one takes into account graphs consisting of disconnected single lines only), then one finds

$$Q_N = \frac{V^N}{N!} \exp \frac{(1/2) N^2}{V} \beta_1,$$

where

$$\beta_1 = \int f(r) d\vec{r},$$

and

$$pV = NkT \left( 1 - \frac{\rho\beta_1}{2} \right). \quad (\text{VI-7})$$

That is, one obtains the correction to the ideal gas law to first order in the density. If one includes clusters of three particles, one obtains the next

term in the density expansion, and so on. There are several ways to treat this in a more systematic way. One is by making use of general theorems from the theory of linear graphs. (Cf. the lectures by Uhlenbeck and Ford quoted in the Introduction, where also the proofs of these theorems are given.)

Theorem I: Let  $G_N$  be a graph of  $N$  points either connected or disconnected. Suppose that with each graph a weight  $W(G_N)$  be associated, which satisfies the following two conditions:

- (a)  $W(G_N)$  is independent of the labeling of the points.
- (b)  $W(G_N)$  is a product of the weights of all connected graphs forming the original graph; i.e.,

$$W(G_N) = \prod_{\ell} W(C_{\ell}),$$

where  $C_{\ell}$  is a connected graph of  $\ell$  points.

Now define:

$$F_N = \sum_{(G_N)} W(G_N),$$

where the summation is over all graphs of  $N$  points, and

$$f_{\ell} = \sum_{(C_{\ell})} W(C_{\ell})$$

where the summation is over all connected graphs of  $\ell$  points. Introduce now the generating functions

$$F(x) = \sum_{N=1}^{\infty} \frac{F_N x^N}{N!},$$

and

$$f(x) = \sum_{\ell=1}^{\infty} \frac{f_{\ell} x^{\ell}}{\ell!}.$$

Then Theorem I says that

$$1 + F(x) = e^{f(x)}. \quad (\text{VI-8})$$

The proof of this theorem is simple though rather abstract, and we will not reproduce it here.

In our case [cf. the expansion (VI-5)], we take

$$W(G_N) = \int \prod_{G_N} f_{ij} d\vec{r}_1 \dots d\vec{r}_N.$$

This definition satisfies the two conditions on the weight mentioned above: it is independent of the labeling of the points because we integrate over all coordinates, and it is the product of the weights of disconnected parts.

Now

$$Q_N = \frac{1}{N!} \sum_{(G_N)} W(G_N),$$

where the summation is over all graphs of  $N$  points. We further introduce the cluster integrals

$$b_\ell(V, T) = \frac{1}{\ell! V} \sum_{(C_\ell)} \prod_{C_\ell} f_{ij} d\vec{r}_1 \dots d\vec{r}_\ell. \quad (\text{VI-9})$$

The factor  $V^{-1}$  is introduced so that for large  $V$  (thermodynamic limit),

$$b_\ell(V, T) \rightarrow \bar{b}_\ell(T), \quad (\text{VI-10})$$

that is, becomes independent of  $V$ .

Theorem I applied to our case gives

$$\sum_{N=0}^{\infty} Q_N z^N = \exp \left\{ \sum_{\ell=1}^{\infty} V b_\ell z^\ell \right\} = \exp [V \chi(V, T, z)], \quad (\text{VI-11})$$

where

$$\chi(V, T, z) \equiv \sum_{\ell=1}^{\infty} b_\ell z^\ell. \quad (\text{VI-12})$$

The relation (VI-11) is called the first Mayer theorem. From the definition (VI-9), we see, for example,

$$b_1 = 1, \quad b_2 = \frac{1}{2!V} \int d\vec{r}_1 d\vec{r}_2 f_{12} = \frac{1}{2!} \int f(r) d\vec{r},$$

$$b_3 = \frac{1}{3!V} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \left[ \bigwedge_1^3 + \bigtriangleup \right], \text{ and } b_4 = \text{cf. last line of (VI-6)}. \quad (\text{VI-13})$$

(3)      (1)

The numbers in parentheses give the number of times the graph has to be counted (e.g., one line can be left out in three different ways).

### 1. Alternative Method

Let us now briefly indicate another derivation, initiated by Ursell, which does not require the assumption of two particle interactions and which moreover can be adapted immediately to the quantum mechanical treatment.

We have

$$Q_N = \frac{1}{N!} \int W_N d\vec{r}_1 \dots d\vec{r}_N,$$

with

$$W_N = e^{-\beta V(\vec{r}_1, \dots, \vec{r}_N)}. \quad (\text{VI-14})$$

In the particular case of pair-wise interactions,

$$W_N = \prod_{i < j} (1 + f_{ij}). \quad (\text{VI-14a})$$

Notice that  $W_N \rightarrow 1$ , if all particles are far apart. Now we define the Ursell cluster functions  $U_\ell$ :

$$U_1(1) \equiv W_1(1) = 1,$$

$$U_2(1, 2) \equiv W_2(1, 2) - W_1(1) W_1(2),$$

$$U_3(1, 2, 3) \equiv W_3(1, 2, 3) - W_2(1, 2) W_1(3) - W_2(1, 3) W_1(2) - W_2(2, 3) W_1(1) \\ + 2W_1(1) W_1(2) W_1(3), \quad (\text{VI-15})$$

and so on. If  $n$  is the number of factors, then the coefficient is

$$(-1)^{n-1} (n-1)!$$

These equations are equivalent to

$$W_1(1) = U_1(1) = 1,$$

$$W_2(1, 2) = U_2(1, 2) + U_1(1) U_1(2),$$

$$W_3(1, 2, 3) = U_3(1, 2, 3) + U_2(1, 2) U_1(3) + U_2(1, 3) U_1(2) + U_2(2, 3) U_1(1) \\ + U_1(1) U_1(2) U_1(3), \quad (\text{VI-16})$$

and so on. We have represented  $W_n$  as a sum of products of  $U$ -functions. A product will contain  $m_\ell$   $U_\ell$ 's where

$$\sum_{\ell=1}^N \ell m_{\ell} = N.$$

It is not difficult to prove that  $U_{\ell}(1, 2, \dots, \ell)$  vanishes for so-called separated configurations, i.e., if the  $\ell$  molecules can be divided into two or more groups that are so far apart that there are no interactions between the groups. The assertion is based on the fact that for separated configurations,  $W_{\ell}$  factorizes. It can be checked in a straightforward way for  $\ell = 1, 2, 3$  and can be proved for the general case by induction.

We now define the cluster integrals,

$$b_{\ell} = \frac{1}{\ell! V} \int U_{\ell}(\vec{r}_1, \dots, \vec{r}_{\ell}) d\vec{r}_1 \dots d\vec{r}_{\ell}. \quad (\text{VI-17})$$

One may verify that for the special case of two-particle interactions, (VI-17) is equivalent to (VI-9), because in  $U_{\ell}$  the disconnected graphs cancel according to (VI-15).

The integral over any product of  $U$  functions in (VI-16) becomes

$$(1!b_1V)^{m_1} \cdot (2!b_2V)^{m_2} \dots = \prod_{\ell} (\ell!b_{\ell}V)^{m_{\ell}}$$

when there are  $m_{\ell}$  clusters of  $\ell$  particles in the products. Remember that

$$\sum_1^N \ell m_{\ell} = N.$$

Other terms in the expansion (VI-16) can be obtained by permutations of molecules, except those within a subgroup (a  $U$ -function), and except also those obtained by permutations of subgroups of equal size. The total number of these terms is then

$$N! \prod_{\ell=1}^N \frac{1}{(\ell!)^{m_{\ell}} m_{\ell}!}. \quad (\text{VI-18})$$

Hence, by integrating  $W_N$  over the coordinates of all particles, we obtain

$$Q_N = \sum_{\substack{\{m_{\ell}\} \\ \sum \ell m_{\ell} = N}} \prod_{\ell} \frac{(Vb_{\ell})^{m_{\ell}}}{m_{\ell}!} \quad (\text{VI-19})$$

where the sum is over all partitions of  $N$  particles, satisfying

$$\sum_1^N \ell m_\ell = N.$$

Relation (VI-19) expresses  $Q_N$  as a sum of products of cluster integrals  $b_\ell$ . Or (in the case of pair-wise interactions) the contribution of the sum of all graphs of  $N$  points is expressed as a sum of products of the contributions of connected graphs only.

The relations (VI-19) can be inverted to

$$Vb_\ell = \sum_{\{n_i\}} (-1)^q q! \prod_i \pi \frac{Q_i^{n_i}}{n_i!}, \quad (\text{VI-20})$$

where

$$q = \sum_{i=1}^{\ell} n_i - 1$$

and  $\sum_{\{n_i\}}$  is the sum over all positive integer combinations  $\{n_i\}$  such that

$$\sum_{i=1}^{\ell} i n_i = \ell.$$

For small indices, one can check (VI-19) and (VI-20) directly from (VI-16) and (VI-15). The first Mayer theorem can now be obtained. If namely (VI-19) or (VI-20) holds, then we have

$$\sum_{N=0}^{\infty} Q_N z^N = \exp \left\{ \sum_{\ell=1}^{\infty} Vb_\ell z^\ell \right\}, \quad (\text{VI-11})$$

i.e., the power series  $\sum_N Q_N z^N$  (remember that  $Q_N \geq 0$ ) can be written

as an exponential. One can verify this by equating coefficients of equal powers of  $z$  successively, but it can be proved generally. Both series should converge.

### Remark

The relation (VI-11) with (VI-19) or (VI-20) is a case of the so-called cumulant expansion in statistics. If  $x$  is a random variable, then

$$\langle e^{\xi x} \rangle = \sum_0^{\infty} \frac{\xi^N \mu_N}{N!} = \exp \left\{ \sum_{\ell=1}^{\infty} \frac{\xi^{\ell} \kappa_{\ell}}{\ell!} \right\},$$

where the moment  $\mu_N = \langle x^N \rangle$ , and the cumulant  $\kappa_{\ell} = \langle x^{\ell} \rangle_{\text{cum}}$ . (The latter average is called a cumulant or connected average.) One can express the cumulants (or semi-invariants) in terms of moments and inversely, and these relations are equivalent to (VI-20) and (VI-19). The cumulant expansion can be extended to the case of several random variables. If these can be divided into two or more statistically independent groups, all cumulants, in which variables of different groups appear, vanish identically.

Actually, in proving (VI-11), we did not need the full cumulant theorem, but only the relations between the coefficients of a certain power series and the coefficients of the power series representing the logarithm of the first one. Brout (cf. Brout and Carruthers, Lectures on Many Electron Problems, Interscience 1963) uses the cumulant theorem in a more complete way by applying it to

$$Q_N = \frac{1}{N!} \int e^{-\beta V} d\tau,$$

which can be considered as an average of an exponential over phase space.  $\log Q_N$  is then expanded in powers of  $\beta$ , but in the coefficients, averages of powers of  $\phi(r)$  occur, which strictly makes no sense. By summing over so-called ladder diagrams, Brout is then able to obtain the virial expansion for  $\log Q_N$ .

We shall now derive the so-called Mayer equations. We have [cf. (VI-11)]

$$\sum_{N=0}^{\infty} Q_N z^N = \exp V\chi(V, T, z). \quad (\text{VI-11})$$



Cauchy's theorem leads to

$$Q_N = \frac{1}{2\pi i} \oint dz z^{-N-1} e^{V\chi}, \quad (\text{VI-21})$$

where  $z^{-N-1}$  decreases strongly along the positive  $z$ -axis, and

$$e^{V\chi} = \sum Q_N z^N$$

is a polynomial in  $z$  with positive coefficients (polynomial, since we can pack only a finite number of particles in a volume  $V$ ). Hence  $e^{V\chi}$  will increase strongly along the positive  $z$ -axis. The integrand of (VI-21) will have a sharp minimum at a certain point  $z_0$  on the positive  $z$ -axis. One may then apply the method of steepest descent. We write the integrand as

$$e^{NK(z)},$$

where

$$K(z) = \frac{V}{N} \chi(V, T, z) - \frac{N+1}{N} \log z.$$

In the thermodynamic limit,

$$N \rightarrow \infty, \quad V \rightarrow \infty, \quad \frac{V}{N} = v, \quad b_\ell(V, T) \rightarrow \bar{b}_\ell(T),$$

[cf. (VI-10)] we assume that

$$\chi(V, T, z) \rightarrow \bar{\chi}(T, z),$$

so that

$$K(z) \rightarrow v \bar{\chi}(T, z) - \log z.$$

Then,

$$K'(z_0) = 0 = -\frac{1}{z_0} + v \left( \frac{\partial \bar{\chi}}{\partial z} \right)_{z=z_0}, \quad (\text{VI-22})$$

and

$$K(z) = K(z_0) + \frac{1}{2} (z - z_0)^2 K''(z_0) + \dots \quad (\text{VI-23})$$

We know from the theory of complex variables (remember the equations of Cauchy-Riemann) that  $K(z)$  has a sharp maximum in  $z_0$  along a line passing through  $z_0$  parallel to the imaginary axis. Then, applying (VI-23),

$$Q_N = \frac{1}{2\pi i} \oint dz e^{NK(z)} = \frac{e^{NK(z_0)}}{\sqrt{2\pi NK''(z_0)}}. \quad (\text{VI-24})$$

One then finds for the free energy per particle

$$f(v, T) = -kT \left[ v \bar{\chi}(T, z_0) - \log \frac{h^3 z_0}{(2\pi mkT)^{3/2}} \right] \quad (\text{VI-25})$$

Hence,

$$p = - \frac{\partial f}{\partial v} = kT \bar{\chi}(T, z_0)$$

[the other terms cancel because of (VI-22)], and from (VI-22),

$$\frac{1}{v} = z_0 \frac{\partial \bar{\chi}(T, z_0)}{\partial z_0}.$$

From the definition of  $\chi$  [cf. (VI-12)], these equations may be written as

$$\left. \begin{aligned} \frac{p}{kT} &= \sum_{\ell=1}^{\infty} \bar{b}_{\ell}(T) z_0^{\ell}, \\ \text{and} \\ \frac{1}{v} &= \sum_{\ell=1}^{\infty} \ell \bar{b}_{\ell}(T) z_0^{\ell}. \end{aligned} \right\} \quad (\text{VI-26})$$

These are the famous Mayer equations.

## 2. The Grand Canonical Ensemble

By means of the grand canonical ensemble, the derivation of the Mayer equations from the first Mayer theorem (VI-11) is almost immediate. Let us therefore digress a moment and consider this ensemble in a little more detail. It can be considered as a collection of canonical ensembles with varying number  $N$  of particles, in a similar way as the canonical ensemble could be considered as a collection of microcanonical ensembles with varying energies.

Suppose we look at a macroscopic subvolume  $V$  of a system enclosed in a large volume  $V'$ . We describe the system by a canonical ensemble. One can then calculate the probability to find, in the sub-volume  $V$ ,  $N$  particles in the phase  $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N, \vec{p}_1, \vec{p}_2, \dots, \vec{p}_N$ . The result is

$$P(N, \vec{r}_1, \dots, \vec{p}_N) = \frac{1}{h^{3N}} \exp\{-\beta pV + \beta N\mu - \beta H(\vec{r}_1, \dots, \vec{p}_N)\}. \quad (\text{VI-27})$$

Here  $p$  is the pressure,

$$\mu = f(v, T) - v \frac{\partial f}{\partial v} = f + pv$$

is the thermodynamic potential (or Gibbs free energy) per particle, and  $\exp(-\beta pV)$  serves as a normalizing factor because necessarily

$$\sum_{N=0}^{\infty} \frac{1}{N!} \int P_N d\vec{r}_1 \dots d\vec{p}_N = 1. \quad (\text{VI-28})$$

The integration includes automatically all permutations of the  $N$  particles over the cells  $d\vec{r}_1 d\vec{p}_1, \dots, d\vec{r}_N d\vec{p}_N$ ; hence we must divide by  $N!$

As a generalization, we now define, for a given kind of particles and for given volume  $V$  and temperature  $T$ , a grand canonical ensemble as an ensemble such that the probability to pick a system of  $N$  particles in the phase  $\vec{r}_1, \dots, \vec{p}_N$  is given by (VI-27). The grand canonical ensemble average of a quantity  $A$  is

$$\langle A \rangle_{\text{gr}} = \sum_N \frac{1}{N!} \int A P_N d\vec{r}_1 \dots d\vec{p}_N. \quad (\text{VI-29})$$

The combined summation and integration can often be performed much more simply than the (canonical) integration alone. In the grand ensemble, the overwhelming majority of systems has a number of particles very close to the average number, so that it leads to very similar results as the canonical ensemble.

The grand canonical partition function is given by [cf. (VI-28)]

$$Z_{\text{gr}} = e^{\frac{pV}{kT}} = \sum_N \frac{1}{N! h^{3N}} \int e^{\frac{N\mu - H}{kT}} d\vec{r}_1 \dots d\vec{p}_N, \quad (\text{VI-30})$$

so that

$$pV = kT \log Z_{gr}. \quad (\text{VI-31})$$

In the thermodynamic limit, one finds that  $(kT/V) \log Z_{gr}$  becomes independent of  $V$ . It will be a function of  $\mu$  and  $T$ . Therefore

$$p = p(\mu, T),$$

or

$$p = p(z, T), \quad (\text{VI-32})$$

where

$$z = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} e^{\mu/kT} \quad (\text{VI-33})$$

is the so-called activity or fugacity. From

$$\mu = f + pv,$$

it follows that

$$\left( \frac{\partial \mu}{\partial p} \right)_T = \left( \frac{\partial f}{\partial v} \right)_T \cdot \left( \frac{\partial v}{\partial p} \right)_T + v + p \left( \frac{\partial v}{\partial p} \right)_T = v,$$

so that

$$\left( \frac{\partial p}{\partial \mu} \right)_T = \frac{1}{v} = \rho. \quad (\text{VI-34})$$

To find the equation of state,  $\mu$  (or  $z$ ) has to be eliminated between (VI-32) and (VI-34).

Let us now return to the first Mayer theorem (VI-11):

$$\sum_{N=0}^{\infty} Q_N z^N = \exp \left\{ \sum_{\ell=1}^{\infty} v \bar{b}_{\ell} z^{\ell} \right\}. \quad (\text{VI-11})$$

From (VI-30) and (VI-33), it appears that the left-hand side of this theorem is just  $Z_{gr}$ . Hence,

$$Z_{gr} = \exp \left\{ \sum_{\ell=1}^{\infty} v \bar{b}_{\ell} z^{\ell} \right\}, \quad (\text{VI-35})$$

and thus,

$$\left. \begin{aligned} p &= \frac{kT}{V} \log Z_{gr} = kT \sum_{\ell=1}^{\infty} \bar{b}_{\ell} z^{\ell}, \\ \rho &= \left( \frac{\partial p}{\partial \mu} \right)_T = \frac{\partial p}{\partial z} \cdot \frac{z}{kT} = \sum_{\ell=1}^{\infty} \ell \bar{b}_{\ell} z^{\ell-1}. \end{aligned} \right\} \quad (\text{VI-26})$$

These are just the Mayer equations (VI-26). Note that (VI-11) above is an identity of two power series, valid for all  $z$  for which both expressions exist. For a particular value  $z_0$  of  $z$ , which is called the activity, the left-hand side of (VI-11) represents the grand canonical partition function. It is this value  $z_0$  of  $z$  which should appear in the Mayer equations (cf. our first derivation of these equations; the index 0 is usually omitted, however).

### B. Virial Expansion of the Pressure

Our problem now is to eliminate  $z$  between the equations (VI-26) in order to arrive at an expansion of  $p$  in powers of the density  $\rho$ , i.e., the so-called virial expansion. This could be done by successive approximation. Remember [cf. (VI-13)] that  $b_1 = 1$ . Therefore, for small  $z$ ,  $\rho = z$ , and the substitution into the first equation (VI-26) yields  $p = kT\rho$ , which is the ideal gas law. Then one could include  $z^2$ , and so on. A systematic method can be applied with the help of another general theorem in graph theory. Just as Theorem I was concerned with a relation between disconnected and connected graphs, Theorem II leads from connected graphs to stars, or from cluster integrals  $b_{\ell}$  to irreducible cluster integrals  $\beta_{\ell}$ .

Theorem II: Let  $W(C_{\ell})$  be the weight corresponding to a connected graph of  $\ell$  labeled points. It should again obey two conditions:

- a)  $W(C_{\ell})$  is independent of the labeling of the points.
- b)  $W(C_{\ell}) = \prod_m W(S_m)$ ,

i.e., it is the product of the weights of all stars forming  $C_{\ell}$ . Now define:

$$f_{\ell} = \sum_{(C_{\ell})} W(C_{\ell}),$$

where the summation is over all connected graphs of  $\ell$  points; and

$$r_m = \sum_{(S_m)} W(S_m),$$

where the summation is over all stars of  $m$  points.

Introducing the generating functions

$$f(z) = \sum_{\ell=1}^{\infty} f_{\ell} \frac{z^{\ell}}{\ell!},$$

and

$$r(y) = \sum_{m=2}^{\infty} r_m \frac{y^m}{m!}$$

(a single point is not a star; therefore  $m$  starts at 2), and calling

$$T(z) = z \frac{df}{dz},$$

then Theorem II states that

$$T(z) = z \exp \left\{ \frac{dr(T)}{dT} \right\}. \quad (\text{VI-36})$$

For a proof, we refer again to the papers of Uhlenbeck cited in the Introduction. To apply Theorem II to our case, we put

$$W(C_{\ell}) = \frac{1}{V} \int \prod_{C_{\ell}} f_{ij} d\vec{r}_1 \dots d\vec{r}_{\ell}.$$

The product property of the weights holds for large  $V$ . Then,

$$f_{\ell} = \ell! b_{\ell}.$$

Further, we define the irreducible cluster integrals ( $m \geq 2$ ):

$$\beta_{m-1} = \lim_{V \rightarrow \infty} \frac{1}{V(m-1)!} \int \sum_{(S_m)} \prod_{S_m} f_{ij} d\vec{r}_1 \dots d\vec{r}_m. \quad (\text{VI-37})$$

Then,

$$r_m = (m-1)! \beta_{m-1}.$$

The generating function is

$$r(y) = \sum_{m=2}^{\infty} \frac{\beta_{m-1}}{m} y^m,$$

so that

$$\frac{dr(y)}{dy} = \sum_{m=1}^{\infty} \beta_m y^m \equiv \phi(y).$$

Further,

$$f(z) = \sum_{\ell=1}^{\infty} b_{\ell} z^{\ell} = \chi(z),$$

and

$$T(z) = z \frac{df}{dz} = \sum_{\ell=1}^{\infty} \ell b_{\ell} z^{\ell} = \rho.$$

Hence Theorem I leads to

$$\rho = z e^{\phi(\rho)}$$

or

$$z = \rho e^{-\phi(\rho)}. \quad (\text{VI-38})$$

The relation (VI-38) inverts the second Mayer equation. It has been derived in various ways by Born and Fuchs, by Kahn and Uhlenbeck, and by others.

We can now obtain the virial expansion. From (VI-26), we have

$$\begin{aligned} \frac{P}{kT} &= \int_0^z \frac{\rho}{z} dz = \int_0^{\rho} e^{\phi(\rho)} d(\rho e^{-\phi(\rho)}) \\ &= \int_0^{\rho} e^{\phi(\rho)} \left\{ e^{-\phi(\rho)} d\rho - \rho \phi'(\rho) e^{-\phi(\rho)} d\rho \right\} \\ &= \rho - \int_0^{\rho} \rho \phi'(\rho) d\rho \\ &= \rho - \int_0^{\rho} \sum_{m=1}^{\infty} m \beta_m \rho^m d\rho \\ &= \rho - \sum_{m=1}^{\infty} \frac{m}{m+1} \beta_m \rho^{m+1}. \end{aligned} \quad (\text{VI-39})$$



If we write, as one does conventionally,

$$\frac{pv}{kT} = 1 + \sum_{m=2}^{\infty} B_m(T) \rho^{m-1}, \quad (\text{VI-40})$$

then the so-called virial coefficients  $B_m$  are

$$B_m(T) = - \frac{m-1}{m} \beta_{m-1}. \quad (\text{VI-41})$$

From (VI-37), it follows that

$$\beta_1 = \frac{1}{V} \int f_{12} d\vec{r}_1 d\vec{r}_2 = \int f(r) d\vec{r} = \frac{1}{V} \int d\vec{r}_1 d\vec{r}_2 \left\{ \begin{array}{c} 2 \\ 1 \end{array} \right\},$$

$$\beta_2 = \frac{1}{2!V} \int f_{12} f_{13} f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \frac{1}{2!V} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \left\{ \begin{array}{c} 3 \\ 1 \quad 2 \end{array} \right\},$$

$$\beta_3 = \frac{1}{3!V} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \left\{ \begin{array}{c} 4 \\ 1 \quad 2 \end{array} \right\} + \begin{array}{c} \text{graph (3)} \\ (3) \end{array} + \begin{array}{c} \text{graph (6)} \\ (6) \end{array} + \begin{array}{c} \text{graph (1)} \\ (1) \end{array},$$

and

$$\beta_4 = \frac{1}{4!V} \int d\vec{r}_1 \dots d\vec{r}_5 \left\{ \begin{array}{c} 4 \\ 1 \quad 2 \end{array} \right\} + \begin{array}{c} \text{graph (12)} \\ (12) \end{array} + \begin{array}{c} \text{graph (60)} \\ (60) \end{array} + \begin{array}{c} \text{graph (10)} \\ (10) \end{array} + \begin{array}{c} \text{graph (10)} \\ (10) \end{array} + \begin{array}{c} \text{graph (60)} \\ (60) \end{array} + \begin{array}{c} \text{graph (30)} \\ (30) \end{array} + \begin{array}{c} \text{graph (30)} \\ (30) \end{array} + \begin{array}{c} \text{graph (15)} \\ (15) \end{array} + \begin{array}{c} \text{graph (10)} \\ (10) \end{array} + \begin{array}{c} \text{graph (1)} \\ (1) \end{array} \right\}.$$

(VI-42)

where the numbers in parentheses indicate the weights of the graphs shown. Analogous to the relation (VI-19) between  $Q_N$  and  $b_\ell$ , there is an explicit relation between  $b_\ell$  and  $\beta_m$ . In fact, one can prove that  $\ell^2 b_\ell$  is the coefficient of  $y^{\ell-1}$  in the expansion of

$$\exp \left\{ \ell \sum_{m=1}^{\infty} \beta_m y^m \right\} = \exp [\ell \phi(y)].$$

Or also,

$$b_\ell = \frac{1}{\ell^2} \sum_{\substack{\{n_m\} \\ \sum m n_m = \ell - 1}} \prod_m \frac{(\ell \beta_m)^{n_m}}{n_m!}. \quad (\text{VI-43})$$

In principle, the virial coefficients can be calculated as soon as the interaction between the particles is known. The computation of all but the very first is, however, a difficult problem of integration. The measured value of the second virial coefficient  $B_2$  is one of the most accurate sources of information for the interaction between molecules. It is known in many cases over a whole range of temperatures within 1% accuracy. Usually, for simple systems, one takes a Lennard-Jones potential

$$\phi(r) = 4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\}. \quad (\text{VI-44})$$

The two parameters  $\epsilon$  and  $\sigma$  can be determined from the experimental  $B_2(T)$ . If energies ( $kT$ ) are expressed in  $\epsilon$  and lengths (volume) in terms of  $\sigma$ , all gases, where the interaction can reasonably be represented by a potential (VI-44), show identical behavior in the classical domain (law of corresponding states). Once the interaction is fixed from  $B_2$ , one can compute  $B_3(T)$ . In several cases, the result obtained fits rather accurately with experiment, which indicates that the underlying assumption of pair-wise interactions is not so bad. For a system of hard spheres, the first few cluster integrals and virial coefficients have the following temperature-independent values (up to  $B_4$ , they have been calculated analytically), where conventionally  $b = 2\pi d^3/3 = 4$  times the volume of the spheres ( $d$  is the diameter):

$$b_1 = 1,$$

$$b_2 = -b,$$

$$b_3 = 1.6875b^2,$$

$$b_4 = -3.554b^3,$$

$$b_5 = 8.420b^4,$$

$$B_2 = b,$$

$$B_3 = (5/8)b^2,$$

$$B_4 = 0.2869b^3,$$

and

$$B_5 = 0.1103b^4. \quad (\text{VI-45})$$

Remember that, for a Van der Waals gas,

$$B_2 = b - \frac{a}{kT},$$

$$B_3 = b^2,$$

$$B_4 = b^3, \text{ etc.} \quad (\text{VI-46})$$

C. A Simplified Cluster Expansion [cf. N. G. van Kampen, *Physica* 27, 783 (1961)]

The derivation of the virial expansion of the equation of state, as reviewed above, is rather complicated. First the partition function  $Q_N$  was written as a sum of contributions from different diagrams. However, we want to find an expansion of the free energy, which is proportional to  $\log Q_N$ , or of the pressure, which is proportional to  $(d \log Q_N)/dV$ . In Mayer's theory,  $p$  was first found as a power series in the activity  $z$ , and after that the result had to be rewritten as a series in the density  $\rho$ .

Van Kampen proceeds by expanding  $Q_N$  in a product (i.e.,  $\log Q_N$  in a series), and in this way obtains the virial expansion directly. In his derivation, there is no need to introduce the activity  $z$ . Let us briefly indicate his procedure. We write

$$\begin{aligned} N!Q_N &= \int e^{-\beta(\phi_{12} + \phi_{13} + \dots + \phi_{N-1,N})} d\vec{r}_1 \dots d\vec{r}_N \\ &= V^N \overline{(\psi_{12}\psi_{13} \dots \psi_{N-1,N})}. \end{aligned} \quad (\text{VI-47})$$

Here,

$$\psi_{12} = e^{-\beta\phi_{12}},$$

and the bar denotes the average over all positions of particles inside  $V$ . Note that  $\psi_{12} \rightarrow 1$  as

$$|\vec{r}_1 - \vec{r}_2| \rightarrow \infty.$$

It will be obvious that, with respect to the averaging,  $\psi_{12}$  and  $\psi_{34}$  are statistically independent, as are  $\psi_{12}$  and  $\psi_{13}$ . We have therefore

$$\overline{\psi_{12}\psi_{13}} = \overline{\psi_{12}}\overline{\psi_{13}} = \overline{\psi_{12}}^2.$$

However,  $\psi_{12}$ ,  $\psi_{13}$ , and  $\psi_{23}$  are not independent in this sense. Still, for small density, one can write in first approximation

$$\overline{\psi_{12} \psi_{13} \psi_{23}} = \overline{\psi}_{12} \overline{\psi}_{13} \overline{\psi}_{23}.$$

This would be exact if one of the  $\psi$ 's were one, but the configurations where all three  $\psi$ 's differ from one are rare for small density.

For a product of  $\psi$ 's involving more than three particles, the same holds. Therefore to first approximation:

$$\begin{aligned} \frac{N! Q_N^{(1)}}{V^N} &= (\overline{\psi}_{12})^{(1/2)N(N-1)} = \left\{ \int e^{-\beta \phi_{12}} \frac{d\vec{r}_1}{V} \frac{d\vec{r}_2}{V} \right\}^{(1/2)N(N-1)} \\ &= \left\{ 1 + \frac{1}{V} \int (e^{-\beta \phi_{12}} - 1) d\vec{r} \right\}^{(1/2)N(N-1)} \\ &= \left\{ 1 + \frac{\beta_1}{V} \right\}^{(1/2)N(N-1)}. \end{aligned} \quad (\text{VI-48})$$

For  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ , such that  $N/V = \rho$ ,

$$\begin{aligned} \frac{1}{N} \log Q_N^{(1)} &= \log V - \log N + 1 + \log \left\{ 1 + \frac{\beta_1}{V} \right\}^{\frac{N-1}{2}} \\ &= \log v + 1 + (1/2) \rho \beta_1. \end{aligned} \quad (\text{VI-49})$$

For the free energy per particle, one finds in first approximation

$$f^{(1)} = -kT \left\{ 1 + \log v + (3/2) \log \frac{2\pi mkT}{h^2} + (1/2) \rho \beta_1 \right\}. \quad (\text{VI-50})$$

To find the higher terms in the virial expansion, one applies successive correction factors, which take account of the statistical correlations between the  $\psi$ 's that were neglected in the foregoing approximation.

The first correction comes from three-particle correlations. One must therefore multiply by

$$\frac{\overline{\psi_{12} \psi_{13} \psi_{23}}}{\overline{\psi}_{12} \overline{\psi}_{13} \overline{\psi}_{23}} = \frac{\overline{\psi_{12} \psi_{13} \psi_{23}}}{\overline{\psi}_{12}^3}.$$

There are  $\binom{N}{3}$  triplets; hence, this factor must be raised to the power  $\binom{N}{3}$ . The first correction factor is therefore

$$\left\{ \frac{1 + 3\overline{f}_{12} + 3\overline{f}_{12}^2 + \overline{f}_{12}\overline{f}_{13}\overline{f}_{23}}{1 + 3\overline{f}_{12} + 3\overline{f}_{12}^2 + \overline{f}_{12}^3} \right\}^{(1/6)N(N-1)(N-2)}$$

Now it is easy to verify that  $\bar{f}_{12} \propto V^{-1}$  and  $\overline{f_{12}f_{13}f_{23}} \propto V^{-2}$ . Thus, in  $(Q_N)^{1/N}$ , one has the correction factor

$$\left(1 + \frac{2\beta_2}{V^2} + O(V^{-3})\right)^{(1/6)(N-1)(N-2)} \rightarrow e^{(1/3) \rho^2 \beta_2}.$$

Therefore, in second approximation:

$$f^{(2)} = -kT \left\{ 1 + \log v + (3/2) \log \frac{2\pi mkT}{h^2} + (1/2) \rho \beta_1 + (1/3) \rho^2 \beta_2 \right\}. \quad (\text{VI-51})$$

In a similar way, one can find the general term, which is

$$\frac{\beta_m}{m+1} \rho^m.$$

In this way, we find for the pressure the result (VI-39)

$$p = -\frac{\partial f}{\partial v} = \frac{kT}{v} \left\{ 1 - \sum_{m=1}^{\infty} \frac{m\beta_m}{m+1} \rho^m \right\}. \quad (\text{VI-52})$$

#### D. Virial Expansion of the Pair Distribution Function

In a similar way as the free energy, the molecular distribution functions can be expanded in powers of the density. These series were first given by Mayer and Montroll, and independently by de Boer and Michels. Van Kampen's method can likewise be applied to this case. Compare his paper where he derives the virial expansion of  $\log g(r)$ . In the supplement of Fisher's book (Ref. 1) the virial expansion of  $\log g(r)$  is derived too.

In the following, we shall use the theorem (IV-14) proved before, that  $g(r)$  is  $(1/2)\rho$  times the functional derivative with respect to the pair potential of the free energy per particle; i.e.,

$$\delta f = (1/2) \rho \int \delta \phi(\vec{r}) g(\vec{r}) d\vec{r}, \quad (\text{VI-53})$$

We have found [cf. (VI-51)]

$$f = -kT \left\{ 1 + \log v + (3/2) \log \frac{2\pi mkT}{h^2} + \sum_1^{\infty} \frac{\beta_m}{m+1} \rho^m \right\}. \quad (\text{VI-54})$$

Hence

$$\delta f = -kT \sum_1^{\infty} \frac{\rho_m}{m+1} \delta \beta_m = (1/2) \rho \int \delta \phi(\vec{r}) g(\vec{r}) d\vec{r}. \quad (\text{VI-55})$$

Let us write

$$g(r) = g^{(0)}(r) + \rho g^{(1)}(r) + \rho^2 g^{(2)}(r) + \dots \quad (\text{VI-56})$$

Equating the coefficients of  $\rho$  in (VI-55), we see that

$$-\frac{kT}{2} \delta \beta_1 \equiv -\frac{kT}{2} \delta \int (e^{-\beta \phi(r)} - 1) d\vec{r} = (1/2) \int \delta \phi(r) g^{(0)}(r) d\vec{r},$$

or

$$g^{(0)}(r) = e^{-\beta \phi(r)}. \quad (\text{VI-57})$$

The coefficient of  $\rho^2$  is found as follows:

$$(1/2) \int \delta \phi(r) g^{(1)}(r) d\vec{r} = -\frac{kT}{3} \delta \beta_2 = -\frac{kT}{6V} \delta \int f_{12} f_{13} f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3;$$

$$\int \delta \phi(r) g^{(1)}(r) d\vec{r} = \frac{1}{V} \int \delta \phi_{12} e^{-\beta \phi_{12}} f_{13} f_{23} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3.$$

Hence,

$$g^{(1)}(r_{12}) = e^{-\beta \phi(r_{12})} \int f_{13} f_{23} d\vec{r}_3 = e^{-\beta \phi(r_{12})} g_1(r_{12}), \quad (\text{VI-58})$$

where

$$g_1(r_{12}) = \int f_{13} f_{23} d\vec{r}_3 = \int d\vec{r}_3 \left\{ \begin{matrix} 3 \\ 1 \quad 2 \end{matrix} \right\}. \quad (\text{VI-59})$$

From

$$\beta_3 = \frac{1}{6V} \int d\vec{r}_1 \dots d\vec{r}_4 \left\{ 3 \begin{matrix} 3 & 4 \\ 1 & 2 \end{matrix} + 6 \begin{matrix} 3 & 4 \\ 1 & 2 \end{matrix} + \begin{matrix} 3 & 4 \\ 1 & 2 \end{matrix} \right\} [\text{cf. (VI-42)}],$$

we can compute  $g^{(2)}(r_{12})$ :

$$\delta \int f_{12} f_{24} f_{34} f_{13} d\vec{r}_1 \dots d\vec{r}_4 = -4\beta V \int \delta\phi_{12} e^{-\beta\phi_{12}} \Phi(r_{12}) d\vec{r}_{12}, \quad (\text{VI-60})$$

where

$$\Phi(r_{12}) = \int f_{13} f_{24} f_{34} d\vec{r}_3 d\vec{r}_4 = \int d\vec{r}_3 d\vec{r}_4 \left\{ \begin{array}{c} 3 \quad 4 \\ \text{---} \quad \text{---} \\ 1 \quad 2 \end{array} \right\}; \quad (\text{VI-61})$$

$$\begin{aligned} \delta \int f_{12} f_{13} f_{23} f_{24} f_{34} d\vec{r}_1 \dots d\vec{r}_4 &= -4\beta V \int \delta\phi(r_{12}) e^{-\beta\phi(r_{12})} \Psi(r_{12}) d\vec{r}_{12} \\ &\quad - \beta V \int \delta\phi(r_{12}) e^{-\beta\phi(r_{12})} \left\{ g_1(r_{12}) \right\}^2 d\vec{r}_{12}, \end{aligned} \quad (\text{VI-62})$$

where

$$\Psi(r_{12}) = \int f_{13} f_{23} f_{24} f_{34} d\vec{r}_3 d\vec{r}_4 = \int d\vec{r}_3 d\vec{r}_4 \left\{ \begin{array}{c} 3 \quad 4 \\ \text{---} \quad \text{---} \\ 1 \quad 2 \end{array} \right\}; \quad (\text{VI-63})$$

and

$$\delta \int f_{12} f_{13} f_{14} f_{23} f_{24} f_{34} d\vec{r}_1 \dots d\vec{r}_4 = -6\beta V \int \delta\phi(r_{12}) e^{-\beta\phi(r_{12})} \chi(r_{12}) d\vec{r}_{12} \quad (\text{VI-64})$$

where

$$\chi(r_{12}) = \int f_{13} f_{14} f_{23} f_{24} f_{34} d\vec{r}_3 d\vec{r}_4 = \int d\vec{r}_3 d\vec{r}_4 \left\{ \begin{array}{c} 3 \quad 4 \\ \text{---} \quad \text{---} \\ 1 \quad 2 \end{array} \right\}. \quad (\text{VI-65})$$

Therefore, if we write

$$g(r) = e^{-\beta\phi(r)} \left\{ 1 + \rho g_1(r) + \rho^2 g_2(r) + \dots \right\}, \quad (\text{VI-66})$$

we have found

$$g_1(r) = \int f_{13} f_{23} d\vec{r}_3 = \int d\vec{r}_3 \left\{ \begin{array}{c} 3 \\ \text{---} \\ 1 \quad 2 \end{array} \right\}, \quad (\text{VI-67})$$



and

$$g_2(r) = \Phi(r) + 2\Psi(r) + (1/2) g_1^2(r) + (1/2) \chi(r) \quad (\text{VI-68})$$



One sees that to find the functions  $g_1(r)$ ,  $g_2(r)$ , etc. we have to break the bonds in  $\beta_2$ ,  $\beta_3$ , etc. From the examples above, it would not be difficult to find the general rule, i.e., the coefficients of the higher powers of  $\rho$  in (VI-66).

#### Remark

If we expand  $\log g(r)$ , that is, if we write

$$\log g(r) = -\beta\phi(r) + \sum_1^{\infty} \rho^n \gamma_n(r), \quad (\text{VI-69})$$

then one easily verifies that

$$\left. \begin{aligned} \gamma_1(r) &= g_1(r) = \int d\vec{r}_3 \left\{ \begin{array}{c} 3 \\ \diagup \quad \diagdown \\ 1 \quad 2 \end{array} \right\}, \\ \text{and} \\ \gamma_2(r) &= g_2(r) - (1/2) g_1^2(r) = \Phi(r) + 2\Psi(r) + (1/2) \chi(r). \end{aligned} \right\} \quad (\text{VI-70})$$

#### E. Computations and Checks on Approximate Expressions for the Pair Distribution Function

For the simple case of hard spheres, one can compute the first few of the functions  $g_n(r)$  in (VI-66);

$$g_1(r) = \int f_{13} f_{23} d\vec{r}_3$$

is very simple; it was first calculated by Kirkwood. One finds (if the diameter of the spheres is taken to be 1)

$$\begin{aligned} g_1(r) &= \frac{2\pi}{3} [2 - (3/2)r + (1/8)r^3], & \text{for } r \leq 2; \\ &= 0, & \text{for } r \geq 2; \end{aligned} \quad (\text{VI-71})$$

$g_2(r)$  for hard spheres has also been computed [cf. Nijboer and Van Hove, Phys. Rev. 85, 777 (1952)]. In particular,  $\chi(r)$  is rather difficult, but it

proved to be possible to express  $\Phi$ ,  $\Psi$ , and  $\chi$  in terms of elementary functions. We will not give the results here.

As soon as one knows  $g(r)$  to a certain order in  $\rho$ , the corresponding virial coefficients can be deduced from it in two alternative ways.

a) We had [cf. (IV-10)]

$$\frac{P}{kT} = \rho - \frac{2\pi}{3kT} \rho^2 \int_0^\infty g(r) r^3 \frac{d\phi}{dr} dr, \quad (\text{VI-72})$$

which we derived from the virial theorem. Further,

$$\frac{P}{kT} = \rho + \sum_{n=2}^{\infty} B_n \rho^n. \quad (\text{VI-73})$$

From these,

$$B_n = -\frac{2\pi}{3kT} \int_0^\infty g^{(n-2)}(r) r^3 \frac{d\phi}{dr} dr = \frac{2\pi}{3} \int_0^\infty g_{n-2}(r) r^3 \frac{df(r)}{dr} dr. \quad (\text{VI-74})$$

For hard spheres,

$$B_n = (2\pi/3) g_{n-2}(1); \quad (\text{VI-75})$$

i.e.,  $B_n$  is given by the value of  $g_{n-2}$  at the diameter of the sphere.

b) From the so-called compressibility integral [cf. (I-4)],

$$1 + 4\pi\rho \int (g(r) - 1) r^2 dr = kT \left( \frac{\partial \rho}{\partial P} \right)_T = \chi_T. \quad (\text{VI-76})$$

For hard spheres, for example, this leads to

$$B_4 = -(1/8) b^3 - \pi \int_1^\infty g_2(r) r^2 dr \quad (\text{VI-77})$$

( $b/4$  is the volume of each particle). Using our result for  $g_2(r)$ , we found from a as well as from b the exact value of  $B_4 = 0.2869b^3$ , as it was computed first by Boltzmann. If we had used some approximate expression for  $g_2(r)$ , the two results obtained from a and b would in general have been

different. It will be obvious that here we have a method to check approximate theories for  $g(r)$  (cf. the paper cited on p. 64).

As an example, let us consider the Born-Green integral equation [cf. (IV-31)]:

$$\frac{1}{\beta} \frac{\partial \log g'(r_{12})}{\partial \vec{r}_1} = - \frac{\partial \phi(r_{12})}{\partial \vec{r}_1} - \rho \int \frac{\partial \phi(r_{13})}{\partial \vec{r}_1} g'(r_{13}) g'(r_{23}) d\vec{r}_3. \quad (\text{VI-78})$$

We write  $g'(r)$  because it is an approximation to the exact  $g(r)$ . Making the substitution,

$$g'(r) = e^{-\beta \phi(r)} v(r),$$

we have

$$\frac{\partial v(r_{12})}{\partial \vec{r}_1} = -\beta \rho v(r_{12}) \int v(r_{13}) v(r_{23}) \frac{\partial \phi(r_{13})}{\partial \vec{r}_1} e^{-\beta \phi(r_{13}) - \beta \phi(r_{23})} d\vec{r}_3. \quad (\text{VI-79})$$

If now one makes the expansion

$$v(r) = 1 + \rho g_1'(r) + \rho^2 g_2'(r) + \dots,$$

introduces this in (VI-79), and equates coefficients of equal powers of  $\rho$ , one finds

$$g_1'(r) = \int f(r_{13}) f(r_{23}) d\vec{r}_3 = g_1(r) \quad (\text{VI-80})$$

[cf. (VI-67)]; i.e.,  $g_1'(r)$  is exact and therefore  $B_3$  is also exact. Furthermore,

$$g_2'(r) = (1/2) g_1^2(r) + \phi(r) + 2\Psi(r) + (1/2) \chi'(r), \quad (\text{VI-81})$$

[cf. (VI-68)] where  $\chi' \neq \chi$ , so that  $g_2$  is given incorrectly. For hard spheres, one can again evaluate  $g_2'(r)$  and compare it with  $g_2(r)$ . When substituted into (VI-74) and (VI-77),  $g_2'(r)$  leads to incorrect and inconsistent values of  $B_4$ . One finds

$$B_{4v}' = 0.2252b^3,$$

and

$$B_{4c}' = 0.3424b^3, \quad (\text{VI-82})$$

where the indices  $v$  and  $c$  stand for virial and compressibility, respectively. This calculation can be extended to  $g'_3(r)$  and  $B'_5$  [cf. Nijboer and Fieschi, *Physica* 19, 545 (1953)]. The result is

$$B'_{5v} = 0.0475b^4,$$

$$B'_{5c} = 0.1335b^4,$$

and

$$B_5 = 0.1103b^4. \quad (\text{VI-83})$$

The exact value was found from Monte Carlo computations. Similar calculations have been performed for other approximate theories for  $g(r)$ , in particular for the so-called hypernetted chain approximation and the Percus-Yevick equation [cf. Refs. (1) and (7)].

The results are compiled in the following table:

	$B_{2v} = B_{2c}$	$B_{3v} = B_{3c}$	$B_{4v}$	$B_{4c}$	$B_{5v}$	$B_{5c}$
Exact	$b$	$(5/8)b^2$	$0.2869b^3$	$0.2869b^3$	$0.1103b^4$	$0.1103b^4$
Born-Green	$b$	$(5/8)b^2$	$0.2252b^3$	$0.3424b^3$	$0.0475b^4$	$0.1335b^4$
Hypernetted chain	$b$	$(5/8)b^2$	$0.4453b^3$	$0.2092b^3$	$0.1447b^4$	$0.0493b^4$
Percus-Yevick	$b$	$(5/8)b^2$	$0.2500b^3$	$0.2969b^3$	$0.0859b^4$	$0.121b^4$

One notes that all these approximate theories start to go wrong with  $g_2(r)$  (or with  $B_4$ ). This, however, does not necessarily mean that these approximations are bad for liquid densities. In successive terms in the virial expansion, there may also be many compensations. For a comparison of exact (computer calculations) and approximate results for high densities, refer to Fisher's book (p. 315 and following).

Let me conclude by making a few remarks only on the hypernetted chain equation and the Percus-Yevick equation. It is possible to derive an exact integral equation for  $g(r)$ . It contains, however, an infinite series. If all but the first term in this series are neglected, one obtains the Percus-Yevick equation. Analogous situations hold for the hypernetted chain and Born-Green approximations. The Percus-Yevick equation can also be obtained from a partial summation of graphs that define  $g(r)$ . In the Percus-Yevick equation, one sums only a small subset of graphs that are included in the hypernetted chain, but apparently they sum to a better approximation (at least for hard spheres and for the Lennard-Jones potential). The relevant summation is exact in the one-dimensional hard-sphere case.

## ACKNOWLEDGMENTS

The lectures published in this report were given for members of the Solid State Science Division of Argonne National Laboratory during part of the academic year 1964-1965, while the author was on leave from the University of Utrecht, Netherlands. He wishes to express his sincere thanks to Dr. O. C. Simpson and the members of the Division, who by many discussions and by their kind hospitality made his stay both profitable and enjoyable.

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